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THE LIGHT TERBIUM ISOTOPES A SURVEY OF HALF-LIVES AND γ-RAY SPECTRA WITH THE USE OF MASS-SEPARATED SAMPLES

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(*Received* 3 *September* 1959)

Abstract—Gadolinium oxide was bombarded with 65 MeV protons to produce terbium nuclides. Following a chemical separation the terbium fraction was mass separated. The different mass samples were studied for their half-lives. γ-Ray spectra were taken in most cases. New information was found concerning γ-rays of the extremely light isotopes, i.e., ^{149}Tb through ^{152}Tb. ^{150}Tb was discovered for the first time in this research. The results obtained on the remaining isotopes are essentially in agreement with the data reported earlier and summarized in the most recent Table of Isotopes (April 1958).

The mass assignments of neutron-deficient isotopes are still uncertain for many elements. The light terbium nuclides provide a good illustration. In 1957, Mihelich *et al.* first reported three new neutron-deficient terbium activities: ^{153}Tb, ^{155}Tb and ^{156m}Tb.[1] After that time, there were still three isotopes with $149 < A < 159$, i.e., ^{150}Tb, ^{152}Tb and ^{157}Tb, for which no half-lives had been reported. Toth *et al.*, in some investigations to be published soon, found the ^{152}Tb half-life to be almost identical to that of ^{151}Tb.[2] The present research was undertaken to isolate samples of each terbium isotope using an electromagnetic isotope separator, and in this way (1) to establish evidence supporting the reported terbium mass assignments and (2) to find the half-life of ^{150}Tb. The latter nuclide was indeed discovered. Its identification is the subject of a brief article.[3]

EXPERIMENTAL PROCEDURE

Approximately 150 mg of gadolinium oxide were bombarded for 4 hr with 65 MeV protons accelerated in the Uppsala synchro-cyclotron. Most of the neutron-deficient terbium nuclides were produced, and a mass separation was performed in order to study the individual isotopes. The isotope separator has been described earlier.[4] A small portion (1–2 mg) of the target was placed in the separator immediately after the material had been delivered (12 hr after the termination of the bombardment). A larger portion (50 mg) was first chemically purified using an ion-exchange technique.[5] The terbium fraction thus obtained was then placed in the mass separator. In this manner, two sets of mass separated samples were prepared: the first samples are labelled "A", and the second, the chemically purified samples, are labelled "B".

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[1] J. W. Mihelich, B. Harmatz and T. H. Handley, *Phys. Rev.* **108**, 989 (1957).
[2] K. S. Toth, K. T. Faler and J. O. Rasmussen, UCRL-8446; *Phys. Rev.* **115**, 158 (1959).
[3] K. S. Toth, S. Bjørnholm, M. H. Jørgensen, O. B. Nielsen and O. Skilbreid, *Phys. Rev.* To be published.
[4] K. O. Nielsen and O. Skilbreid, *Nucl. Instr.* **2**, 15 (1958).
[5] S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. R. Seaborg, *J. Amer. Chem. Soc.* **76**, 6229 (1954).

The ion source of the isotope separator was operated, employing a technique especially applicable to separations of radioactive materials of high specific activity. The method, to be described in more detail elsewhere, is characterized by converting the metal oxide to the corresponding volatile chloride in the ion source itself using carbon tetrachloride vapour. The reaction in the case of gadolinium oxide would be:

$$2Gd_2O_3 + 3CCl_4 \rightarrow 4GdCl_3 + 3CO + 1\tfrac{1}{2}O_2.$$

In the case of the A samples, the charging material used was the bombarded oxide. In preparing the B samples, the solution of terbium isotopes was evaporated to a few drops after the chemical separation and 1 mg of stable gadolinium was added. The solution was transferred to a 5 mm O quartz tube filled with quartz wool. The tube was heated and finally ignited to red heat in a Bunsen burner to evaporate the solution and burn off the organic eluent, leaving the gadolinium oxide finely dispersed on the quartz wool. The tube was then transferred to the ion source. The ions were collected on a thin aluminium plate. After the mass separation, the aluminium was discoloured in discrete strips corresponding to the different stable gadolinium isotopes. The thickness of the active layer is known from previous experience to be a few hundred $\mu g/cm^2$ or less.[6]

γ-Spectra were obtained, using a 100-channel scintillation spectrometer with a 3 in. NaI(Tl) crystal as detector. The decay curves of each mass number were determined by counting the samples in a windowless flow-type proportional counter and in a single channel scintillation spectrometer. The α-activity of the samples was also measured using the flow counter. Only mass 149 showed a significant α-counting rate. Consequently, the decay curves, with the exception of this mass, were measured with the counter operated on the β-plateau. The single channel spectrometer was set so as to accept all γ-rays corresponding to energies higher than 65 keV. The only exception to this was mass 150, where the bias was set to accept only γ-rays over 450 keV in energy.

EXPERIMENTAL RESULTS

(1) *General*

Fig. 1 shows the activity measured for samples A and B in the proportional counter on various days, plotted as a function of the mass number. A comparison of the plots for samples A and B reveals the effectiveness of the chemical purification carried out prior to the mass separation of the B samples. While, in the A series, mass 159 displays a high counting rate due to the presence of gadolinium 159, the activity of the same mass number in the B series has decreased by a factor of approximately 50. The activity of mass 156 in each series is used as reference.

Most of the terbium activity is seen to be distributed among isotopes with masses from 151 to 156. Such a distribution of activities is reasonable, considering the isotopic abundance of gadolinium, and the fact that at the bombarding energy (65 MeV) the most probable (p, xn) reaction will be $(p, 4n)$, $(p, 5n)$ and $(p, 6n)$. The radioactivity of the B samples diminishes with time in accordance with the known terbium half-lives. The longer-lived ^{155}Tb and ^{156}Tb display a relatively higher counting rate than the shorter-lived ^{151}Tb, ^{152}Tb, ^{153}Tb, and ^{154}Tb with the passage of time.

One other point must be made. The two extreme masses shown in Fig. 1B, 144 and 162, would not be expected to exhibit any activity since they could not be produced in the bombardment. The activity present at these mass positions is due to a general smearing of the total activity during the mass separation.[4] This "smearout" activity was found in mass numbers 144, 148, 158 and 162, and had identical decay curves in each case. It is therefore assumed to be present at all mass numbers. In addition to this general "smear-out" activity, the finite mass resolution of the isotope separator has to be taken into account.[4] Decay curve analyses revealed that, for a

[6] K. O. Nielsen, *Proceedings of the Harwell Isotope Conference*, Chap. 9 (1955).

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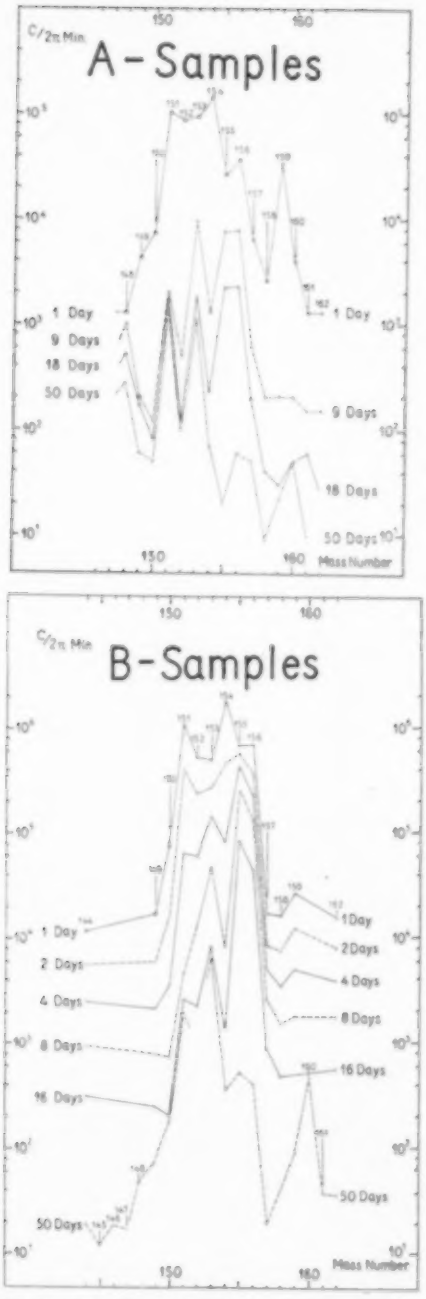

FIG. 1.—Diagram of β-activity vs. mass number. Part A represents the mass-separated samples of the proton bombarded gadolinium target. Part B represents the mass-separated terbium activities from the same target.

Curves measured at various time intervals after the separation. The activities are measured with a windowless flow-type proportional counter operated on the β-plateau. The counting rate as a function of mass number is correct only within a factor of two. The counting rate as a function of time, however, is accurate to 2 per cent.

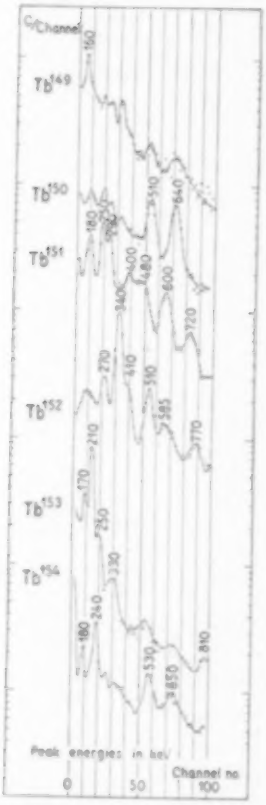

FIG. 2.—γ-Spectra of A samples recorded 1–5 hr after mass separation (13–17 hr after termination of cyclotron bombardment). Peaks that are seen to belong to terbium isotopes of the masses indicated are labelled with energies. The effect of the mass separation is clearly demonstrated. The isotope enrichment factor is about thirty. Detector: 3 × 3 in. NaI-crystal connected with a 100-channel pulse-height analyser.

given mass number, 2–5 per cent of its activity was present in the two neighbouring isotopes. The presence of neighbours was particularly noticeable in those cases where the isotope of interest had low abundance, e.g., ^{151}Tb contamination in mass 150. Table 1 lists the half-lives determined from the decay curves after correction of all background effects. In almost all cases the corrected decay curves were linear over two or three decades.

Fig. 2 is a series of γ-ray spectra for ^{149}Tb through ^{154}Tb, all taken at the same energy setting of the scintillation spectrometer. For a given spectrum, in Fig. 2 only

TABLE 1.—HALF-LIVES

Isotope	Sample A		Sample B		Weighted mean
	Flow counter	γ-Counter	Flow counter	γ-Counter	
^{149}Tb			4·10 ± 0·05* hr		4·10 ± 0·05 hr
^{150}Tb			3·0 ± 0·2 hr	3·2 ± 0·2 hr†	3·1 ± 0·2 hr
^{151}Tb	17 ± 1 hr		16·4 ± 0·8 hr	18·0 ± 0·8 hr	17·5 ± 0·7 hr
^{152}Tb	17·3 ± 0·4 hr	18 ± 1 hr	17·6 ± 0·4 hr	17·2 ± 0·4 hr	17·4 ± 0·3 hr
^{153}Tb	2·30 ± 0·05 days	2·15 ± 0·15 days	2·33 ± 0·05 days	—	2·30 ± 0·05 days
^{154m}Tb	8·4 ± 0·2 hr	—	8·6 ± 0·2 hr		8·5 ± 0·2 hr
^{154}Tb	20·2 ± 0·7 hr	—	21·2 ± 0·5 hr	—	21·0 ± 0·5 hr
^{155}Tb	—	—	5·4 ± 0·2 days	—	5·4 ± 0·2 days
^{156}Tb	—	—	5·05 ± 0·1 days	5·12 ± 0·1 days	5·1 ± 0·1 days
^{157}Tb	—	—	<4 hr or >10 yr	—	
^{158}Tb	—	—	<4 hr or >10 yr	—	
^{159}Gd	18·5 ± 0·5 hr			—	18·5 ± 0·5 hr

* Flow counter operated at the α-plateau. In all other cases the counter was set on the β-plateau.
† γ-Counter biased to accept only γ-rays of energy higher than 450 keV. In all other cases the bias corresponded to $E_\gamma >$ 65 keV.

those peaks that belong to the particular mass number are labelled with energies. The series of spectra illustrates the mass separation achieved. Several other γ-ray spectra were obtained in addition to the ones shown. Table 2 gives a list of energies and relative intensities of the γ-rays found. The intensities have been corrected for crystal efficiency, but not for internal conversion.

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(2) *Individual isotopes*

We shall now discuss the individual samples with respect to their half-lives and the γ-rays observed.

^{149}Tb. This isotope has an α/E.C. branching ratio of about 10 per cent,[7] so that α-particles emitted by the isotope were easily detectable. The α-decay curve yielded a single half-life of 4·10 ± 0·05 hr, in excellent agreement with the adopted ^{149}Tb half-life.

It was difficult to resolve a 4 hr half-life from the mass 149 decay curve taken at the β-plateau, because the larger percentage of activity was due to the general "smear-out" mentioned above. A short half-life of the order of 5 hr could be resolved, presumably representing ^{149}Tb. The ratio of α- to $(\alpha + \beta)$-activity was found to be 0·16 ± 0·04.

One γ-ray can be assigned with certainty to the decay of ^{149}Tb, viz., 160 keV. In addition, there are indications of possible γ-rays belonging to ^{149}Tb at about 125, 350 and 400 keV.

^{150}Tb. The mass 150 decay curves were found to contain, besides ^{151}Tb and the

[7] L. Winsberg (UCRL), Abstract for the American Physical Society Meeting, December (1958).

"smear-out" activity, a 3·1 hr ± 0·2 half-life which was recognized as a new isotope, namely ^{150}Tb. A lengthier discussion concerning this nuclide has already been published.[3] Only three peaks could be assigned with certainty to ^{150}Tb, viz. 510 (annihilation radiation?), 640 and 930 keV.

From α-systematics in the rare-earth region, ^{150}Tb is expected to be an α-emitter. Its α-decay energy should be approximately 3·7 MeV and its α/E.C. branching ratio

TABLE 2.—γ-RAY ENERGIES AND RELATIVE INTENSITIES*

Isotope	E_γ keV	I_γ (arb. units)	Isotope	E_γ (keV)	I_γ (arb. units)
^{149}Tb	(125)	weak	^{152}Tb	1320	~5
	160	80	(cont.)	(1600)	
	(350)	(100)		(1820)	
	(400)	weak		(2380)	
^{150}Tb	510	100		(2700)	
	640	100	^{153}Tb	87·5‡	35
	930	35		110†	40
^{151}Tb	108‡	90		170†	30
	180†	50		212‡	100
	252‡	100		(250)	weak
	288‡	100		(330)	weak
	400	~60		(810)	weak
	440	~50	^{151m}Tb	123‡	Due to the presence of
	480	~80	and ^{154}Tb	180	two half-lives it is not
	600	100		248‡	possible to give any
	720	~80		300	meaningful intensities.
	870	~40		347‡	
^{152}Tb	271‡	10		530	
	344‡	100		650	
	410‡	~ 5	^{155}Tb	85	100
	585‡	10		105	90
	770	~ 5		155	35
	960	~ 5		260	~10
	1110	~ 5		360	~5

* The intensities are corrected for crystal efficiency, but not for internal conversion.
† Line known from conversion electron measurements to be double.
‡ Energy accurately determined from conversion line measurements.[1,9,10]

should be between those of ^{149}Tb (0·1) and ^{151}Tb (10^{-6}).[8] The present investigation did not reveal any α-activity that could be assigned to ^{150}Tb; limit: $\alpha/\alpha + \beta < 5 \times 10^{-4}$.

^{151}Tb. A half-life of 17·5 ± 0·7 hr was found for this isotope. The following γ-ray peaks were assigned to the decay of ^{151}Tb: 108, 180, 252, 288, 400, 440, 480, 600, 720 and 870 keV. The first four γ-rays have been identified by means of their conversion electrons in some earlier works.[1,9] The 180 keV peak is known to be

[8] K. S. TOTH and J. O. RASMUSSEN (UCRL). Unpublished.
[10] K. S. TOTH, Thesis, University of California (1958).

made up of two γ-rays whose energies are, 180·1 and 192·0 keV. The remaining γ-rays have been identified for the first time in this investigation. It is quite possible that some or all of the new γ-rays are in reality double.

γ-γ-Coincidence measurements were performed and, although numerous coincidence relations were found, the measurements could not be interpreted unambiguously and a decay scheme for ^{151}Tb could not be established.

^{152}Tb. The half-life of ^{152}Tb was found to be 17·4 $\pm$ 0·3 hr, i.e., almost identical to that of ^{151}Tb. The following γ-rays are assigned to the decay of ^{152}Tb: 271, 344,

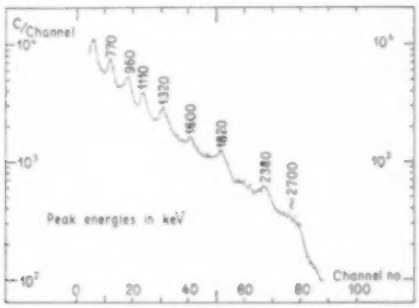

FIG. 3.—High energy γ-ray spectrum of ^{152}Tb.

410, 585, 770, 960, 1110 and 1320 keV. In addition, γ-ray peaks were seen at approximately 1600, 1820, 2380 and 2700 keV. All the ^{152}Tb γ-ray transitions, with the exception of the 344 keV peak, have been identified for the first time. Fig. 3 shows the high energy ^{152}Tb γ-ray spectrum. A study of the decay of ^{152}Tb was performed, using a six-gap β-spectrometer and coincidence techniques. This study will be published separately.[10] Part of the γ-energies given above are taken from the conversion-line measurements (see footnote ‡, Table 2).

^{153}Tb. A half-life of 2·30 $\pm$ 0·05 days was found for ^{153}Tb. The γ-ray peaks assigned to ^{153}Tb were 87·5, 110, 170 and 212 keV. These transitions have been identified earlier by accurate conversion-electron studies.[1,9] From the latter it is known that the 110 and 170 keV peaks each consist of two γ-rays, viz. 102·3 and 109·9 keV, and 170·6 and 174·5 keV, respectively. No new γ-rays could be identified with certainty for this isotope, though there were indications of possible ones at 250, 330 and 810 keV.

^{154}Tb. Two half-lives were found for ^{154}Tb, i.e., 8·5 $\pm$ 0·2 hr and 21·0 $\pm$ 0·5 hr. The investigation thus confirms the existence of an isomeric state in ^{154}Tb, as previously reported.[1,11] γ-Rays observed were 123, 180, 248, 300, 347, 530, and 650 keV.

^{155}Tb. A half-life of 5·4 $\pm$ 0·2 days was determined for ^{155}Tb. γ-Ray peaks were observed at 85, 105, 155, 260 and 360 keV. No higher energy γ-rays could be assigned to ^{155}Tb decay.

^{156}Tb. The half-life of ^{156}Tb was found to be 5·1 $\pm$ 0·1 days. The presence of shorter-lived radiation was observed, but no precise resolution of this half-life was possible. The half-life seemed to be between 5 and 12 hr. The evidence thus supports the existence of an isomeric state in ^{156}Tb. No γ-ray spectrum was obtained for ^{156}Tb.

[10] K. S. Toth, O. B. Nielsen and O. Skilbreid, *Nucl. Phys.* To be published.
[11] T. H. Handley and W. S. Lyon, *Phys. Rev.* **99**, 1415 (1955).

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Masses 157 *and* 158. No half-lives were identified that could be assigned to either ^{157}Tb or ^{158}Tb. The 5 days half-life of ^{156}Tb was seen in the decay curves of mass 157. γ-Ray spectra also indicated that ^{156}Tb was present in this case. (The ^{156}Tb γ-rays are known from an earlier work.[12]) Rough limits can be put on the possible half-lives of masses 157 and 158. If one assumes the same counting efficiencies in the flow counter and the same production rates during the bombardment for the masses 153, 156, 157 and 158, one arrives at upper and lower limits of 100–250 years and 2 hr, respectively. A more realistic statement would be $t_{\frac{1}{2}}$: ^{157,158}Tb, < 4 hr or > 10 years.

Mass 159. The $18{\cdot}5 \pm 0{\cdot}5$ hr ^{159}Gd activity was seen at this mass number in the A samples.

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The zealous assistance during the measurements of Mrs. H. NORDBY, Miss E. R. JOHANSEN, and Mr. G. SIDENIUS is gratefully acknowledged.

[13] P. GREGERS-HANSEN, O. B. NIELSEN and R. K. SHELINE, *Nucl. Phys.* **12**, 389 (1959).

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J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 8 to 13. Pergamon Press Ltd. Printed in Northern Ireland

THE MASS-YIELD CURVE FOR FISSION OF ^{237}Np BY 14·5 MeV NEUTRONS

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Abstract—The mass yield curve for the fission of ^{237}Np by 14·5 MeV neutrons has been determined. Also an absolute yield of 4·94 per cent for ^{99}Mo was measured and used to normalize the mass-yield curve. The shape of the curve is very similar to the ^{235}U and ^{238}U fission-yield curves with neutrons of the same energy. The chief difference is the smaller peak-to-trough ratio which for neptunium is approximately 4·4. Brief details of the separation schemes and counting methods are given.

THIS paper describes the determination of the yields of nineteen fission product chains in the fission of ^{237}Np by 14·5 MeV neutrons. This is the first fission yield curve to be published at any energy for neptunium. The distribution curve has the familiar double peak with a peak-to-trough ratio of approximately 4·4. This compares with 6·4, 4·8 and 3·6 for the peak-to-trough ratio of ^{238}U, ^{235}U and ^{239}Pu in fission by 14 MeV neutrons.[1]

EXPERIMENTAL

Preliminary purification of neptunium

The neptunium oxide was known to contain about 0·05 per cent plutonium and practically no uranium. The plutonium contamination was reduced to a very low level before irradiating by separating the neptunium and plutonium on an anion exchange resin. In 11 M hydrochloric acid containing 5 per cent hydriodic acid Np^{4+} and Np^{5+} are strongly absorbed on to anion exchanger whilst Pu^{3+} is not absorbed and is readily washed off the column. The neptunium is readily removed with 4 M hydrochloric acid. The effluent is converted to neptunium nitrate and then decomposed at 800°C to leave pure neptunium dioxide.

Irradiations

Samples of about 200 mg of pure neptunium dioxide were irradiated for 2 or 3 hr in a flux of 14·5 MeV neutrons from the (D,T) reaction produced by bombarding a zirconium tritide target with 500 keV deuterons.

Two methods of irradiation were employed. In the first, neptunium samples were irradiated close to the neutron source in a large (5×10^9 sec^{-1} cm^{-2}) but unmeasured neutron flux in order to measure various fission yields relative to that for ^{99}Mo. In the second, neptunium samples were placed in a known, but necessarily smaller, neutron flux in order to find the absolute fission yield of ^{99}Mo. The neutron flux was found by placing the samples in a known geometry with respect to the neutron source and determining the output of the source by counting the α-particles associated with the (D,T) reaction. A proportional counter subtending a small solid angle at the source and placed at an angle of 135° to the deutron beam direction, was used to count the α-particles.

Errors in the fission yields due to activation by low energy neutrons were negligible. In an earlier paper,[2] it was concluded that the thermal and epithermal neutrons were less than 3×10^{-5} per cent of the 14 MeV flux and that the neutrons of about 1–3 MeV were present to the extent of approximately 1 per cent of the 14 MeV flux. These results are valid for this work as the same irradiation geometry was used.

[1] A. W. PROTOPOPOV *et al.*, *Atomnaya Energiya* **8**, 130 (1958).
[2] J. L. PERKIN, L. P. O'CONNOR and R. F. COLEMAN, *Proc. Phys. Soc.* **72**, 505 (1958).

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The neptunium oxide samples were in the form of disks some 100 mg cm^{-2} thick. To ensure the recovery of fission products escaping from the surface of the sample, aluminium catcher-foils were used to sandwich the neptunium oxide. Neglect of this precaution could have caused an error of about 10 per cent in the determination of the absolute yield of ^{99}Mo.

Chemical separation and purifications

The fission products required in this investigation fell conveniently into two groups. One group containing the shorter lived activities was processed after standing for 2 hr. The other group stood

TABLE 1

Np Sr, Ba, Y, R.E.s, Zr, Mo, Pd, Ag, Cd.

10 M HCl
Amberlite column

effluent	adsorbed
Fraction 1. Sr, Ba, Y, R.E.s, Ag.	Np, Zr, Mo, Pd, Cd.

6 M HCl

effluent	adsorbed
Fraction 2. Zr.	Np, Mo, Pd, Cd.

1 M HCl

effluent	adsorbed
Fraction 3. Mo, Np.	Pd, Cd.

1 M NH_4OH

effluent

Fraction 4. Pd, Cd.

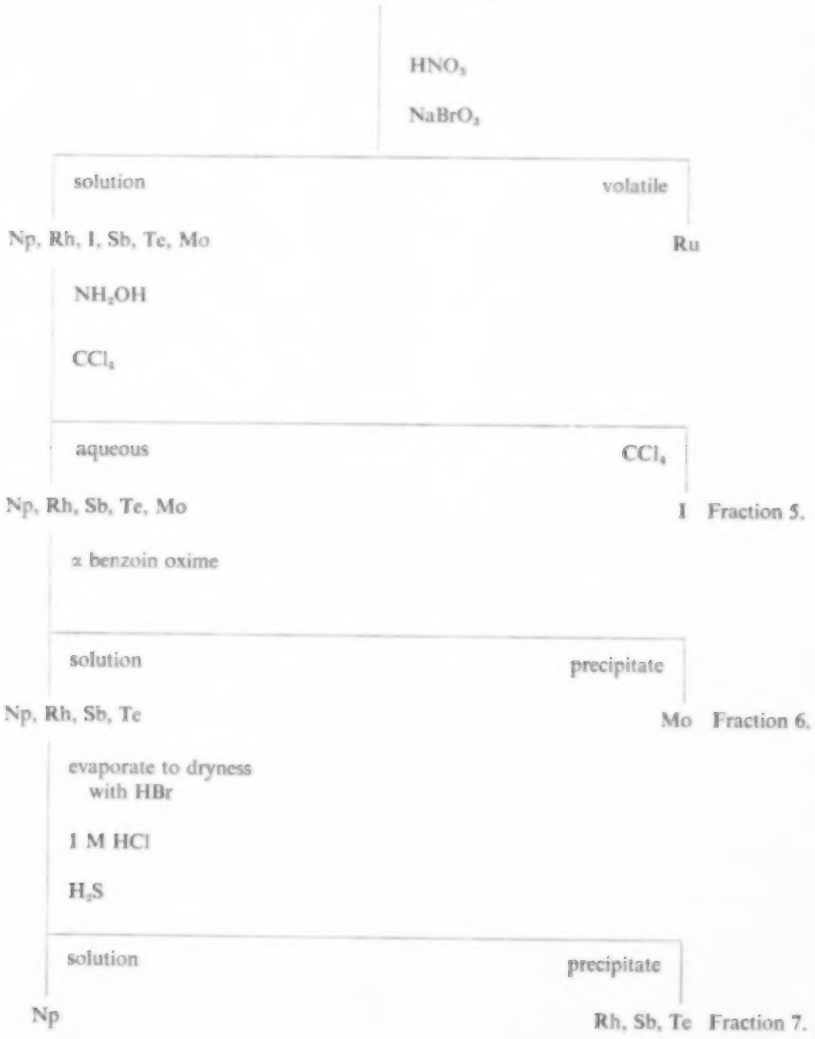
for 24 hr to allow the percursors to decay before separating the desired fission products. The separations used in this work were based on well tried schemes developed for studying the fission of uranium and plutonium at A.W.R.E. Only minor modifications were necessary to give satisfactory separations from neptunium and its daughter protoactinium.

The irradiated neptunium was added to 1 mg each of strontium, barium, yttrium, zirconium, molybdenum, palladium, silver, cadmium and rare earth carriers in *aqua regia* and evaporated to dryness. The residue was dissolved in 10 M hydrochloric acid and transferred to an Amberlite CG 400 anion exchange column (particle size about 30 μ). The carriers were separated into four fractions as indicated in Table 1, using data obtained from KRAUS and MOORE.[2]

[2] K. KRAUS and F. MOORE, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 113. United Nations, New York (1956).

Fraction 1. Silver was separated by diluting the solution with water to precipitate silver chloride. Purification of the silver was achieved by repeated sulphide and chloride precipitations followed by the reduction to silver metal with hydrazine. Yttrium and the rare earths were first separated as hydroxides and then the cerium was precipitated as ceric iodate. The remaining rare earths were

TABLE 2



separated on a cation exchanger using α-hydroxy isobutyric acid as eluting agent. Strontium and barium were separated as carbonates, purified by precipitation from fuming nitric acid and then separated from each other on a zirconium tungstate column. The zirconium tungstate was prepared by the method of KRAUS *et al.*[1] Strontium was eluted with 1 M ammonium chloride and barium with 3 M ammonium chloride.

[1] K. KRAUS, T. A. CARLSON and J. S. JOHNSON, *Nature, Lond.* **177**, 1128 (1956).

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Fraction 2. Zirconium was scavenged with neodymium from a fluoride solution and then precipitated as barium fluozirconate. The zirconium was extracted from 6 M hydrochloric acid by thenoyl trifluoroacetone in benzene and then back extracted into fluoride solution.

Fraction 3. Molybdenum was separated from neptunium by precipitation with α-benzoin oxime and further purified by scavenging with neodymium hydroxide and oxime precipitations.

Fraction 4. The cadmium and palladium sulphides were precipitated and then cadmium sulphide was dissolved in 2 M hydrochloric acid leaving palladium unattacked. Cadmium was purified by scavenging with antimony sulphide from 2 M hydrochloric acid and then diluting to precipitate cadmium. Palladium was purified by extracting the α-furildioxime complex into chloroform.

In the second separation scheme the irradiated neptunium was added to 1 mg of rhodium, iodine, antimony, tellurium and molybdenum carriers. The solution was warmed with sodium bromate to oxidize the iodine to iodate and also to oxidize ruthenium which volatilized off. The solution was then reduced with hydroxylamine.

Fraction 5. The iodine was purified by repeated carbon tetrachloride extraction cycles.

Fraction 6. The molybdenum was purified as in fraction 3.

Fraction 7. Tellurium sulphide was precipitated from 9 M hydrochloric acid/2M pyridine solution leaving rhodium and antimony in solution. On reducing the acidity to 2 M the antimony precipitated and on warming the solution rhodium sulphide came down.

The tellurium was further purified by scavenging with neodymium hydroxide and then precipitating elementary tellurium with sulphur dioxide. The antimony was purified by extracting antimony pentachloride from 7 M hydrochloric acid into iso-propyl ether. The rhodium fraction was scavenged with silver chloride, adsorbed on an anion exchange column from 0·1 hydrochloric acid, and then eluted with 6 M acid.

The final purified solutions of these fission products was divided into two portions. One portion was transferred to a thin plastic foil (20 μ g cm^{-2}) for counting and the second portion was used for the chemical yield determination using the methods of HERRINGTON and MONK.[5]

Counting procedure

Each fission product was counted in a 4π proportional counter for a sufficient time to determine the purity of the nuclide separated. The sources were sufficiently thin to make the errors due to the absorption and scattering of β-particles very small. In the case of about half the nuclides separated the growth of the activity of a daughter had to be taken into account. To do this the necessary data concerning decay schemes and branching ratios were taken from the compilations of STROMINGER *et al.*[6] and KATCOFF.[7]

RESULTS

The fission yields given in Table 3 and Fig. 1 were measured relative to the yield of ^{99}Mo. Each yield is the mean of three independent determinations from different irradiations and the error quoted represents the total spread of the individual results. The yields and errors are normalized to a value of 4·94 per cent for ^{99}Mo.

Absolute yield for ^{99}Mo

The absolute yield of ^{99}Mo was determined in two different ways. In the first, neptunium samples were irradiated in known neutron fluxes as already described. The results of these experiments together with the best available value for the fission cross-section enabled the absolute yield of ^{99}Mo to be calculated. A fission cross-section of 2·4 $\pm$ 0·2 barns for 14·6 MeV neutrons has been reported by PROTOPOPOV *et al.*[8] and one of 2·5 $\pm$ 0·07 barns for 14·0 MeV neutrons has been measured by

[5] J. HERRINGTON and R. G. MONK, UKAEA Report AWRE 0-39/56.
[6] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).
[7] S. KATCOFF, *Nucleonics* No. 4, **16**, 78 (1958).
[8] A. N. PROTOPOPOV, IU. A. SELITSKII and S. M. SOLOV'EV, *Atomnaya Energiya* **4**, 190 (1958).

TABLE 3

Element	Mass number	Fission yield
Sr	91	2·71 ± 0·25
Y	93	4·94 ± 0·25
Zr	97	5·43 ± 0·49
Mo	99	4·94
Rh	105	3·50 ± 0·20
Pd	109	1·48 ± 0·25
Pd	112	1·23 ± 0·05
Ag	111	1·23 ± 0·05
Cd	115	1·23 ± 0·05*
Sb	127	2·52 ± 0·15
Te	132	4·29 ± 0·74
I	131	3·55 ± 0·59
Ba	139	4·84 ± 0·35
Ba	140	4·89 ± 0·35
Ce	143	3·60 ± 0·74
Nd	147	1·73 ± 0·25
Sm	153	0·32 ± 0·025
Eu	157	0·094 ± 0·030
Gd	159	0·069 ± 0·030

* A 10 per cent correction has been made to this yield to take into account the yield of ^{115m}Cd.

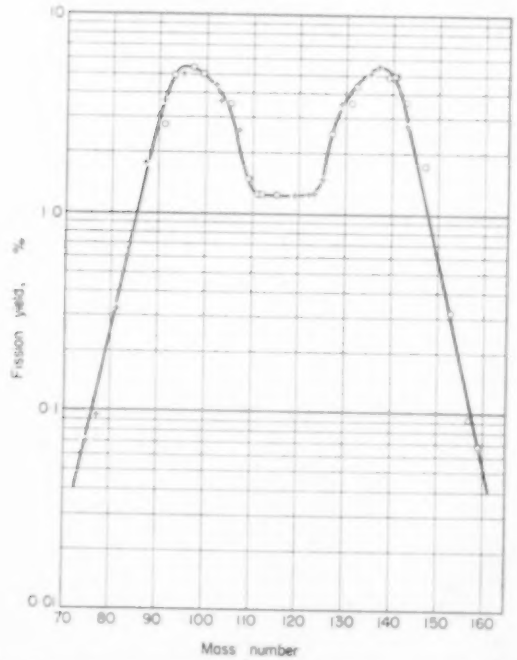

FIG. 1.—The mass-yield curve for the fission of ^{237}Np with 14·5 MeV neutrons.
○ Experimental point. + Mirror image point.

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MOAT.[9] The more precise value at the slightly lower neutron energy was used in the present calculation.

In the second method the relative mass yield curve was normalized to a total yield of 200 per cent. In order to draw a smooth and symmetrical curve, mirror image points were calculated and to do this a knowledge of the average number of neutrons emitted per fission, $\bar{\nu}$, was required. Mirror image points based on a value of $\bar{\nu} \sim 4{\cdot}5$ gave the best fit to a symmetrical curve through the experimental points. The precision of this method of determining $\bar{\nu}$ was in this particular instance no greater than $\pm$15 per cent. The value of the absolute yield of ^{99}Mo calculated from the mass-yield curve was however very insensitive to this uncertainty in $\bar{\nu}$. It is of interest to note that from the systematics of the variation of $\bar{\nu}$ for spontaneous fission with atomic weight and the variation of $\bar{\nu}$ with excitation energy, both of which are approximately linear, (FRASER[10]) a value of approximately 4·7 for $\bar{\nu}$ can be predicted. The drawing of a smooth curve through the experimental points ignores the possibility of fine structure in the fission yield curve. There is insufficient experimental evidence to indicate the presence or otherwise of fine structure.

The results from the absolute yield determinations from these two methods are given as follows:

Per cent absolute yield of ^{99}Mo (absolute neutron flux determination)	4·97 $\pm$ 0·2*
(mass yield curve determination)	4·90 $\pm$ 0·2
Mean value	4·94 $\pm$ 0·2

CONCLUSION

In general the mass-yield curve found for neptunium is similar to those of ^{235}U and ^{238}U and ^{239}Pu for the same neutron energy. The chief difference is the different peak-to-trough ratio which for neptunium is approximately 4·4.

* The error quoted here includes that of the fission cross section assumed in the calculation.

[9] A. MOAT, *J. Nucl. Energy* To be published.

[10] J. S. FRASER, Atomic Energy of Canada Ltd. Report CRP–642–A, p. 239 (1956).

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 14 to 20. Pergamon Press Ltd. Printed in Northern Ireland

LATTICE ENERGIES AND ASSOCIATED PROPERTIES OF SOME CRYSTALLINE CYANIDES

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Abstract—The lattice energies and enthalpies of hydration of a number of monovalent and divalent cyanides have been calculated. The free energies of solution of these compounds, ΔG_s°, and the free energies of hydration, ΔG_h°, for the corresponding ions have been evaluated.

RECENTLY the free energies of solution of a number of monovalent and divalent metallic halides[1] and monovalent nitrates[2] have been calculated. In this paper the calculations are extended to a series of metallic cyanides. The relevant thermodynamic relationships are:

$$\Delta G_s^\circ = \Delta H_s^\circ - T\Delta S_s^\circ$$
$$= \Delta H_s^\circ - T(\Sigma \bar{S}_i^\circ - S_L^\circ) \quad (1)$$

where ΔG_s°, ΔH_s° and ΔS_s° are the standard molar free energy, enthalpy and entropy of solution respectively. $\Sigma \bar{S}_i^\circ$ is the sum of the "absolute" partial gram-ionic entropies of the hydrated ions, and may be calculated as previously described from the relative entropies of LATIMER[3]; S_L° is the molar entropy of the lattice which is also listed by LATIMER. Throughout this paper T° refers to the temperature 298·16°K; the enthalpy and free energy terms, and $T\Delta S_s^\circ$, are in kcal/mole, and entropies are in cal/mole degree.

In Table 1 the free energies of some cyanides are listed; these have been calculated from the enthalpies and entropies reported in the literature.[4,5]

TABLE 1.—FREE ENERGIES OF SOLUTION OF SOME CYANIDES

	ΔH_s°	$\Sigma \bar{S}_i^\circ$	S_L°	$T\Delta S_s^\circ$	ΔG_s°
NaCN	0·3	42·6	14·7	8·3	−8·0
KCN	2·8	52·7	16·4	10·8	−8·0
$Ca(CN)_2$	−13·5	43·2	21·3	6·5	−20·0
$Ba(CN)_2$	−2·8	53·4	25·7	8·3	−11·1
$Cd(CN)_2$	−8·7	41·8	24·9	5·0	−13·7
$Hg(CN)_2$	3·6	51·0	27·4	7·0	−3·4

The values of ΔG_s° for sodium, potassium and calcium cyanides are in general agreement with those to be expected from their known solubilities; this correspondence is not obtained, however, with the cyanides of barium and cadmium. In the case

[1] M. F. C. LADD and W. H. LEE, *Trans. Faraday Soc.* **54**, 35 (1958).
[2] M. F. C. LADD and W. H. LEE, *J. Inorg. Nucl. Chem.* **13**, 218 (1960).
[3] W. M. LATIMER, *Oxidation Potentials*. Prentice Hall, N.J. (1956).
[4] F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE, N. B. S. Circ. No. 500 (1952)
[5] E. LANGE and W. MARTIN, *Z. Phys. Chem.* A **180**, 233 (1937).

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of cadmium, this might be related to its known tendency to form complex ions in solution; it was considered advisable to calculate the enthalpies of solution, in these cases, and we have included in this calculation the cyanides of zinc and silver, for which experimental enthalpies of solution are not available.

The calculation of ΔH_s° involved the following stages:

1. The lattice energy and enthalpy of potassium cyanide were calculated by means of the equation previously formulated:[1]

$$U(r_0) = \frac{N}{10^3 J} \cdot \left[\frac{Ae^2}{r_0} \left(\frac{\rho}{r_0} - 1 \right) + \frac{C}{r_0^6} \left(\frac{6\rho}{r_0} - 1 \right) + \frac{D}{r_0^8} \left(\frac{8\rho}{r_0} - 1 \right) + \frac{9\, h\nu_{\max}}{4} \right] \text{kcal/mole} \qquad (2)$$

in which $\dfrac{\rho}{r_0} = \dfrac{(Ae^2/r_0 + 6C/r_0^6 + 8D/r_0^8)}{(9V_0/\beta + 2Ae^2/r_0 + 42C/r_0^6 + 72D/r_0^8)}$.

Potassium cyanide was chosen because the following accurate structural data were available:

Equilibrium interionic distance, r_0, = 2·64 Å.[6]

Compressibility, β, = 5·92 × 10^{-12} reciprocal barye.[7]

$C = 400 \times 10^{-60}$ erg cm^6/molecule, $D = 500 \times 10^{-76}$ erg cm^8/molecule; these coefficients have been estimated from a consideration of ionic polarizabilities.[8]

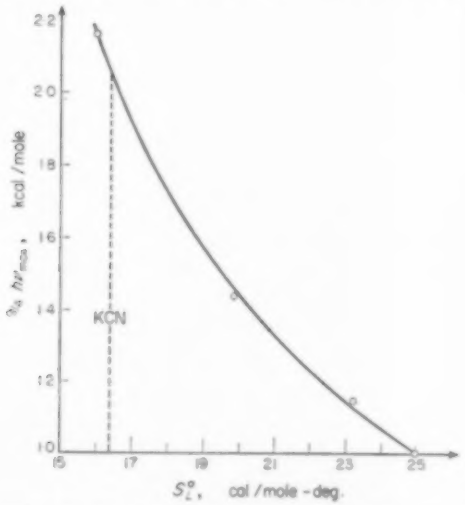

FIG. 1.—Interpolation for the determination of the zero-point energy of potassium cyanide.

The lattice energy $U(r_0)$ of potassium cyanide so calculated was −161 kcal/mole, from which the lattice enthalpy ΔH_l° = −162 kcal/mole. The zero-point energy term in equation (2) was evaluated by a procedure due to WADDINGTON[9]; in Fig. 1, the

[6] *Index of X-ray Diffraction Data*, A.S.T.M. (1958).
[7] P. BRIDGMAN, *Proc. Amer. Acad. Arts Sci.* **76**, 71 (1948).
[8] J. R. TESSMAN, A. H. KAHN and W. SHOCKLEY, *Phys. Rev.* **92**, 890 (1953).
[9] T. C. WADDINGTON, Thesis, Cambridge (1955).

zero-point energies of the potassium halides have been plotted against their lattice entropies (S_L°), and the zero-point energy for potassium cyanide was obtained by interpolation, taking the lattice entropy as 16·4 (Table 1).

2. The value of ΔH_l° so obtained was used in the modified Born–Haber cycle represented by equation (3) to obtain the composite term $\Delta H_f^\circ(CN^-)_{gas}$, which corresponds to the enthalpy of formation of the gaseous cyanide ion:

$$\Delta H_l^\circ = \Delta H_f^\circ - S_M - I_M - \Delta H_f^\circ(CN^-)_{gas} \qquad (3)$$

The significance of these terms, and the sources of data, have been considered previously.[1,10] The value obtained was: $\Delta H_f^\circ(CN^-)_{gas} = 13$ kcal/g-ion. Taking the value of $\Delta H_f^\circ(CN)_{gas}$ as 94 kcal/mole,[11] the electron affinity of the CN radical, E(CN) = −81 kcal.

3. From this value for $\Delta H_f^\circ(CN^-)_{gas}$ and other appropriate thermodynamic data, the lattice energies of the remaining cyanides were calculated from equation (3), and are listed in Table 2.

TABLE 2.—LATTICE ENERGIES AND ENTHALPIES OF SOME CYANIDES

	$-\Delta U_l^\circ$ [$=U(r_o)$]	$-\Delta H_l^\circ$		$-\Delta U_l^\circ$	$-\Delta H_l^\circ$
NaCN	178	179	$Ba(CN)_2$	479	481
KCN	161	162	$Zn(CN)_2$	667	669
AgCN	221	222	$Cd(CN)_2$	609	611
$Ca(CN)_2$	529	531	$Hg(CN)_2$	649	651

The lattice energies of the alkali-metal cyanides have been calculated previously; the results are summarized in Table 3. The results of SHERMAN[12] were obtained by

TABLE 3.—CALCULATED LATTICE ENERGIES OF ALKALI-METAL CYANIDES

	SHERMAN	WADDINGTON (i)	WADDINGTON (ii)	YATSIMIRSKII	Present work
LiCN	—	—	—	192	—
NaCN	169	174	170	179	178
KCN	155	158	157	162	161
RbCN	149	151	150	155	—
CsCN	141	139	142	149	—

the application of the Born–Landé equation. However, the values for the repulsion exponent n, which depend upon the compressibility, must be empirical, since compressibilities are reported only for potassium cyanide.

WADDINGTON's two sets of values[13] are obtained (i) using the simple Born–Mayer treatment, and (ii) using HUGGINS's equation, taking $\rho = 0{\cdot}345$ in each case, as did HUGGINS for the alkali halides. We find the value $\rho = 0{\cdot}317$ for potassium cyanide,

[10] M. F. C. LADD and W. H. LEE, *J. Inorg. Nucl. Chem.* **11**, 264 (1959).
[11] L. BREWER, L. K. TEMPLETON and F. J. JENKINS, *J. Amer. Chem. Soc.* **73**, 1462 (1951).
[12] J. SHERMAN, *Chem. Rev.* **61**, 93 (1932).
[13] T. C. WADDINGTON, in *Advances in Inorganic Chemistry and Radiochemistry* (Edited by H. J. EMELÉUS and A. G. SHARPE) p. 197. Academic Press, New York (1959).

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and in general ρ is not a constant even in the relatively more simple alkali halides, as the following values show:[10]

	LiCl	NaCl	RbCl	CsCl	KF	KCl	KBr	KI
$\rho =$	0·345	0·332	0·333	0·313	0·311	0·342	0·355	0·373

We find it difficult to understand WADDINGTON's values, since in our experience neglecting the London dispersion energy results in a more positive value for the lattice energy, which is true here only of cesium cyanide.

YATSIMIRSKII's[13,14] results agree with ours, and indeed the value for $\Delta H_f^\circ(CN^-)_{gas}$ deduced from his lattice energies is also 13 kcal/g-ion. To some extent this agreement is fortuitous, since his lattice energies are derived from KAPUSTINSKII's formula,[15] and the "thermochemical radius" of the cyanide ion. The latter quantity is dependent for its evaluation also upon the KAPUSTINSKII equation, and thus the general objections to the latter[10,13] apply equally here. YATSIMIRSKII's thermochemical radius for the cyanide ion is 1·82 Å, whereas the effective radius in the "rock salt" structures is 1·94 Å, and the additivity of this and the Pauling cationic radii is well upheld in potassium, rubidium and cesium cyanides. It is clear that the reduction of an r_0 value from 1·96 Å to 1·82 Å has, in the case of sodium and potassium cyanides, about the same effect as the application of the more complete equation.

4. The lattice energies and enthalpies of solution of the silver and thallium halides and of some divalent halides were combined with the experimentally determined free energies of hydration of the halide ions[16] in order to obtain the free energies and enthalpies of hydration of the cations. The results obtained from this procedure are listed in Table 4.

5. From the experimentally determined free energies of hydration of the sodium and potassium ions,[16] the value calculated above for the calcium ion, and the enthalpies of solution of their cyanides,[4] the enthalpy of hydration of the cyanide ion was obtained. Table 5 lists these results.

Mean values: $\Delta H_h^\circ(CN^-) = -72{\cdot}8$ kcal/g-ion.

$\Delta G_h^\circ(CN^-) = -68{\cdot}3$ kcal/g-ion.

Anomalous results were obtained for mercuric cyanide; these are discussed later.

6. The sum of the enthalpies of hydration of the cyanide ion and of a cation M^+ is the enthalpy of hydration of the cyanide, $\Delta H_h^\circ(MCN)$; this was calculated for each compound. Hence from equation (1), and the relationship: $\Delta H_s^\circ = \Delta H_h^\circ - \Delta H_l^\circ$, the enthalpies and free energies of solution of these cyanides were determined. The calculation of ΔH_s° by this method is permissible only if the enthalpy of formation of the crystalline cyanide is known independently of its enthalpy of solution, which is the case for the cyanides of silver, barium, zinc and cadmium.[17,18,19] The data are recorded in Table 6.

[14] K. B. YATSIMIRSKII, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 453 (1947).
[15] A. F. KAPUSTINSKII, *Quart. Rev. Chem. Soc.* **10**, 283 (1956).
[16] J. E. B. RANDLES, *Trans. Faraday Soc.* **52**, 1573 (1956).
[17] J. THOMSEN, *Thermochemische Untersuchungen*. J. A. Barth, Leipzig (1882–3).
[18] A. JOANNIS, *Ann. Chim. Phys.* **26**, 482 (1882).
[19] H. H. FRANCK and H. BANK, *Z. Elektrochem.* **40**, 699 (1934).

Table 4.—The free energies and enthalpies of hydration of some cations

	$-\Delta H_l^\circ$(MX)	ΔH_s°(MX)	$-\Delta H_h^\circ$(MX)	$-\Delta H_h^\circ(X^-)$	$-\Delta H_h^\circ(M^+)$	$-\Delta G_h^\circ(M^+)$
AgF	227	−4·9	231·9	108·6	123·3	115·3
AgCl	215	15·9	199·1	76·1	123·0	114·8
AgBr	212	20·1	191·9	69·2	122·7	114·5
AgI	209	26·7	183·3	60·2	123·1	114·9
				Mean	123	115
TlCl	174	10·4	163·6	76·1	87·5	82·4
TlBr	170	13·7	156·3	69·2	87·1	82·0
TlI	165	17·7	147·3	60·2	87·1	82·0
				Mean	87	82
CaF_2	621	3·2	618	217·2	401	384
$CaCl_2$	533	−19·8	553	152·2	401	384
$CaBr_2$	512	−26·3	538	138·4	400	383
CaI_2	490	−28·7	519	120·4	399	382
				Mean	400	383
BaF_2	564	0·9	563	217·2	346	332
$BaCl_2$	494	−3·1	497	152·2	345	331
$BaBr_2$	477	−6·1	483	138·4	345	331
BaI_2	452	−11·4	463	120·4	343	329
				Mean	345	331
$ZnCl_2$	643	−17·1	660	152·2	508	486
$ZnBr_2$	630	−16·1	646	138·4	508	486
ZnI_2	613	−13·2	626	120·4	506	484
				Mean	507	485
CdF_2	659	−8·7	668	217·2	451	431
$CdCl_2$	599	−4·4	603	152·2	451	431
$CdBr_2$	590	−0·7	591	138·4	453	433
CdI_2	574	1·3	573	120·4	453	433
				Mean	452	432
$HgCl_2$	624	3·2	621	152·2	469	461
$HgBr_2$	618	3·4	615	138·4	477	469

Table 5.—The enthalpy, entropy and free energy of hydration of the cyanide ion

	ΔH_s°	$-\Delta H_h^\circ$	$-\Delta G_h^\circ(M^+)$	$-\Delta H_h^\circ(M^+)$	$-\Delta H_h^\circ(CN^-)$	$-\Delta S_h^\circ(CN^-)$[a]	$-\Delta G_h^\circ(CN^-)$
NaCN	0·3	178·7	98·2	106·0	72·7	15·2	68·2
KCN	2.8	159.2	80.6	85.9	73.3	15.2	68.8
$Ca(CN)_2$	−13·5	545	383	400	72·5	15·2	68·0

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TABLE 6.—THE ENTHALPIES AND FREE ENERGIES OF SOLUTION OF SILVER, BARIUM, ZINC AND CADMIUM CYANIDES

	$-\Delta H_f^\circ$	$-\Delta H_h^\circ$	ΔH_s°	ΣS_i°	S_L°	$T\Delta S_s^\circ$	ΔG_s°
AgCN	222	196	26	45·9	20·0	7·7	18·3
$Ba(CN)_2$	481	491	−10	59·4	25·7	10·0	−20·0
$Zn(CN)_2$	669	653	16	30·9	22·9	2·4	13·6
$Cd(CN)_2$	611	598	13	41·8	24·9	5·0	8·0

TABLE 7.—AN ATTEMPTED EVALUATION OF $\Delta H_h^\circ(Hg^{2+})$

	$-\Delta H_f^\circ$	ΔH_s°	$-\Delta H_h^\circ$	$-2\Delta H_h^\circ(X^-)$	$-\Delta H_h^\circ(Hg^{2+})$
$HgCl_2$	624	3·2	621	152·2	469
$HgBr_2$	618	3·4	615	138·0	477
$Hg(CN)_2$	651	3·6	647	146.0	501

DISCUSSION

ΔG_s° is seen to give a good account of the variations in solubility within this series. Thus, the value calculated from ΔG_s° for the molar solubility of silver cyanide is $2{\cdot}0 \times 10^{-7}$ in good agreement with the value $2{\cdot}1 \times 10^{-7}$ determined potentiometrically.[20] Again, the value of ΔG_s° for cadmium cyanide recorded in Table 5 is in accordance with its known low solubility.[21]

The values obtained for the enthalpy and free energy of hydration of the cyanide ion from mercuric cyanide (−90·8 and −67·8 kcal/g-ion respectively) are at variance with the values recorded in Table 5. The mercuric ion in combination with the chloride, bromide or cyanide ions does not show a constant hydration enthalpy at infinite dilution, as Table 7 shows. It seems clear that this departure from additivity is related to the non-electrolyte character of these compounds in solution, and considerable doubt arises with regard to the general applicability of the quantities $\Delta H_f^\circ(Hg^{2+}\text{ aq.})$ and $S_i^\circ(Hg^{2+}\text{ aq.})$ to solutions of mercuric compounds. Thus there is some uncertainty in the value of ΔG_s° for $Hg(CN)_2$ listed in Table 1, although from its known solubility[21] it appears to be not unreasonable.

It is of interest to compare the cyanides of certain cations with the corresponding chlorides and bromides. Considering the sodium and potassium salts, ΔH_s° and S_L° are similar for both series, and the lower ΔG_s° of the cyanides, leading to increased solubility, reflects the greater entropy of the aqueous cyanide ion:

$$T\Delta S_s^\circ(CN^-) - T\Delta S_s^\circ(Cl^-) = 5 \text{ kcal/g-ion and}$$
$$T\Delta S_s^\circ(CN^-) - T\Delta S_s^\circ(Br^-) = 4 \text{ kcal/g-ion.}$$

The free rotation of the cyanide ion,[22] which confers spherical symmetry upon it in these compounds, is presumably maintained in solution, so that the increased entropy of solution must arise from the greater structure-breaking effect of this ion, as compared with the halide ions, upon water.

[20] K. MASAKI, *Bull. Chem. Soc. Japan* **5**, 345 (1930).
[21] A. SEIDEL, *Solubility of Inorganic Compounds*. Van Nostrand, New York (1952).
[22] R. C. EVANS, *Crystal Chemistry*. Cambridge (1948).

With the silver salts the increased lattice energy of the cyanide, due to its larger homopolar component, counteracts this entropy difference, and the cyanide is less soluble than the chloride or bromide. The lower solubilities of zinc and cadmium cyanides are similarly explained. These are yet further examples of the increased stability of crystal lattices in which the cation is of the "non inert gas" type.

It may be noted that the positive values of ΔH_f°(cryst) for silver cyanide (+34·9), zinc cyanide (+18·4), cadmium cyanide (+39·0) and mercuric cyanide (+62·0) show that these compounds are thermodynamically unstable with regard to formation from their elements. However, because of the lower energy state of the crystal with respect to the aqueous ions (for example; ΔG_s° AgCN = +18·3 kcal/mole) these solids may be prepared by precipitation.

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FLUOROSULPHONIC ACID—III

THE HEATS OF FORMATION OF THE ANHYDROUS AND AQUEOUS ACIDS

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Abstract—The heat of formation of anhydrous fluorosulphonic acid, determined by mixing solutions of hydrogen fluoride and sulphur trioxide in fluorosulphonic acid, was -184 ± 1–2 kcal. The heat of formation of the aqueous acid, from the heat of hydrolysis, was 5·9 kcal greater. Some heats of reaction involving sulphur trioxide are compared. The reported heat of formation of chlorosulphonic acid is incompatible with the above heats of reaction.

THE heat of formation of fluorosulphonic acid has not been recorded. It is of interest for comparison with related solvents and because of its potential use for solution calorimetry.

A value cannot be obtained from the heat of hydrolysis because two hydrolytic reactions occur simultaneously.[1]

$$HSO_3F + H_2O = H_3O^+ + SO_3F^- \quad (1)$$

$$HSO_3F + 4H_2O = 3H_3O^+ + SO_4^{2-} + F^- \quad (2)$$

The heats of formation of anhydrous and aqueous fluorosulphonic acids cannot be calculated from the single heat of reaction. Thus a reaction involving fluorosulphonic acid needs to be measured under anhydrous conditions.

The first reaction tried was the replacement of chlorine in chlorosulphonic acid with anhydrous hydrogen fluoride, but this was difficult to complete.

The second reaction was the formation of fluorosulphonic acid from anhydrous hydrogen fluoride and a solution of sulphur trioxide in fluorosulphonic acid. This method was also unsuitable because of the difficulties in controlling the flow of hydrogen fluoride and cooling losses by evaporation of solution.

The method finally adopted was to mix solutions of hydrogen fluoride in fluorosulphonic acid with solutions of excess sulphur trioxide in the same solvent. A Pyrex glass calorimeter could be used to measure this heat of reaction and the heat of solution of sulphur trioxide in fluorosulphonic acid. The heat of formation of the aqueous acid could then be found by deducting the heat due to reaction (2) from the total heat of hydrolysis.

EXPERIMENTAL DETAILS AND RESULTS

All heats of reaction were measured at 25°C.

Heat of reaction of HF *with* HSO_3Cl

HSO_3Cl (1·5–4 g) in a platinum tube (1·5 cm diameter, 20 cm length) was immersed in 500 ml of water contained in a Dewar vessel fitted with a Beckmann thermometer.

[1] A. A. WOOLF, *J. Chem. Soc.* 2840 (1954).

Hydrogen fluoride was condensed into a polythene test tube and passed by means of a dry air stream through a steel spiral in the thermostat (25·0 ± 0·05°) into the platinum tube until no further temperature rise was observed (20–60 min). A residue analysed after 20 min passage of hydrogen fluoride contained 6 per cent of the initial chlorine either as unchanged HSO_3Cl or HCl in solution. Hydrogen fluoride was also retained in solution unless the air passage was prolonged. The mean heat of reaction per mole of HSO_3Cl was 9·5 ± 1 kcal.

Heat of reaction of SO_3 *in* HSO_3F *with excess* HF

HF was passed through HSO_3F till saturation and then into a solution of SO_3 (1·6 g) in HSO_3F (3·2 g) in the platinum tube for 10 min. The residue contained a large excess of HF (2·1 g) over that required for reaction with SO_3. The heat evolved was $14{\cdot}0_4$ kcal/mole of SO_3.

Heat of reaction of HF *with excess* SO_3

The SO_3 solutions were prepared by distilling SO_3 from 40 per cent oleum into HSO_3F and weighing the receiver before and after. The HF solutions were made similarly by passing HF from a cylinder into a platinum bottle containing HSO_3F. To avoid loss of HSO_3F the HF was initially passed through a saturated solution of HF in HSO_3F. The composition of some HF solutions was checked by analyses for fluorine. The analytical values were within 2 per cent of the values found by direct weighing. The latter were taken as the more reliable in view of the difficulties in analysis.

The "Pyrex" glass calorimeter was designed for 60 ml of liquid. It consisted of a Dewar vessel the open end of which was a B50 cone. The head was made from a B50 socket fitted with a central stirrer, which rotated on a ground glass bearing surface, and three symmetrically and radially placed B10 sockets. Through two of the sockets were fitted glass pockets for a heater and thermistor. The third was reserved for addition of reactants. The temperature change was followed with the thermistor (resistance 1,576·0 Ω at 25°C). The smallest heat change was equivalent to a 50 Ω change in resistance. The HF solution was added from a tapless weight pipette. The surfaces exposed to HF were of polythene. The pipette was filled with the solution above 25°. With care, spillage of solution could be avoided without the presence of a tap. The weight pipette and contents were allowed to attain 25° in the thermostat before fitting to the calorimeter head. The water equivalent of the calorimeter was found by applying 6 V to a resistance (14·65 Ω) for periods of from 3–10 min. An averaged value per gramme of solution from fourteen runs was used to obtain the values given in Table 1.

Heat of solution of SO_3 *in* HSO_3F

The SO_3 was distilled into a special ampoule which could be inserted in the calorimeter head and the thin-walled end pierced in situ.

Heat of hydrolysis

Thin walled glass bulbs containing HSO_3F were broken under 500 ml of water in the simple Dewar flask calorimeter. The hydrolysate was analysed immediately by titration in the cold with standard alkali. The fraction hydrolysed according to

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TABLE 1.—HEAT OF REACTION OF HF AND EXCESS SO_3 IN HSO_3F SOLUTION

Initial solution (g)		Solution added (g)		Final ratio (M)	Heat evolved/mole HSO_3F formed. (kcal)
HSO_3F	SO_3	HF	HSO_3F	HSO_3F/SO_3	
97·6	7·69	0·208	4·41	11·39	12·9
96·4	6·43	0·417	3·44	16·21	13·7
101·6	5·24	0·361	2·25	16·94	12·9
100·4	8·05	0·387	3·66	12·36	14·0
*106·0	7·50	0·559	5·29	16·11	13·7

* The final composition of this solution was checked by analysis for fluorine (Found 25·8 per cent; calc. 26·2 per cent)

TABLE 2.—HEAT OF SOLUTION OF SO_3 IN HSO_3F

HSO_3F (g)	SO_3 (g)	HSO_3F/SO_3 (M)	Heat evolved/mole SO_3 (kcal)
103·3	2·104	39·3	1·35
103·3	1·483	55·9	1·41

TABLE 3.—HEAT OF HYDROLYSIS OF HSO_3F

H_2O (g)	HSO_3F (g)	Fraction hydrolysed	H_2O/HF (M)	Heat evolved/mole HSO_3F (kcal)
498	2·064	0·490	2·760	24·1
489	2·313	0·519	2·307	25·2
499	1·395	0·418	4·780	21·8

equation (2) is $(3R - 1)/2$ where R is the ratio of the titre obtained to the titre expected for complete hydrolysis. It has been shown previously that Pyrex glass can be used for dilute acid solutions containing hydrofluoric acid.[2]

All the auxiliary heats of formation are taken from the National Bureau of Standards Circular 500 (1952).

DISCUSSION

The average heat evolved when a mole of hydrogen fluoride solution was mixed with excess of sulphur trioxide solution was $13·4 \pm 0·5$ kcal. The large deviations observed were mainly caused by difficulties in the manipulation of the hydrogen fluoride solutions. The heat of formation of anhydrous fluorosulphonic acid can be calculated from this heat, together with the heats of solution of hydrogen fluoride and sulphur trioxide in fluorosulphonic acid, and the heat of dilution of fluorosulphonic acid in a dilute solution of sulphur trioxide in fluorosulphonic acid. The

[2] A. A. WOOLF, *J. Chem. Soc.* 231 (1951).

last was considered small enough to neglect. The heat of solution of sulphur trioxide measured directly was 1·4 kcal. An approximate heat of solution of hydrogen fluoride, 0·6 kcal, follows indirectly as the difference between the heat of reaction of sulphur trioxide in fluorosulphonic acid with excess of hydrogen fluoride, and the heat of reaction of solutions of hydrogen fluoride and sulphur trioxide with the latter in excess. The heat of formation of fluorosulphonic acid so calculated was $-184{\cdot}_3$ kcal.

The calculation of the heat of formation of the aqueous acid is set out in Table 4.

TABLE 4

Fraction hydrolysed by equation (2)	Total heat evolved (H)	Final dilution of acid (HF or H_2SO_4)	Heat calc. for reaction (2)/mole	Fraction of total heat due to (2)(h)	Heat of hydration ($H - h$)
0·418	21·8	4·780	38·4	16·0	5·8
0·490	24·1	2·760	37·2	18·2	5·9
0·519	25·2	2·307	37·2	19·3	5·9

The heat of formation of a mole of aqueous fluorosulphonic acid at dilutions from 2300 to 4700 moles of water was $-190{\cdot}_2$ kcal.

The heat of formation of a dilute solution of sodium fluorosulphonate, $204{\cdot}_6$ kcal, follows from the previously measured heat of neutralization.[1]

An approximate value for the heat of formation of chlorosulphonic, $-132{\cdot}_7$ was obtained from the rough measurements on the heat of the reaction

$$HSO_3Cl + HF = HSO_3F + HCl$$

This value should not be in error by more than 4 kcal/mole; the present value differs by 10 kcal/mole from OGIER's[3] value (−142·7). If the latter value were the correct one the displacement reaction would be endothermic rather than exothermic.

The heats of reaction of sulphur trioxide are collected in Table 5.

TABLE 5

Reactant	Product	Heat evolved (kcal)
H_2O	H_2SO_4	20·9
HF	HSO_3F	15·4
HCl	HSO_3Cl	6·0
*HCl		16·0
HBr	No reaction	—
H_2SO_4	$H_2S_2O_7$	4·1
HSO_3F	HS_2O_6F(?)	1·4

* OGIER's value

[3] J. OGIER, *C.R. Acad. Sci., Paris* **92**, 922 (1881).

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The hydrogen halide sequence again indicates that OGIER's value is in error. The small heat of reaction with fluorosulphonic acid agrees with previous evidence from conductivity measurements for the absence of a sharp distinction between the acids HSO_3F and HS_2O_6F.[4] The only evidence for the latter is the isolation of its potassium salt.[5]

The heat of hydration of fluorosulphonic acid is surprisingly low compared with that of sulphuric (23·0) or hydrofluoric acids (14·5). This, together with the small heat of ionization of fluorosulphonic acid, would indicate a simpler ionization and suggest that species other than hydroxonium and fluorosulphonate ions are present in very small concentrations.

Acknowledgement—This work was carried out in 1954 during the tenure of a Turner and Newall Fellowship at Manchester University.

[4] A. A. WOOLF, *J. Chem. Soc.* 433 (1955).
[5] H. A. LEHMANN and L. KOLDITZ, *Z. Anorg. Chem.* **272**, 73 (1953).

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THE VAPOUR PRESSURE OF URANIUM TETRAFLUORIDE

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Abstract—The vapour pressure of liquid uranium tetrafluoride was measured between 4 and 180 mm Hg (1018–1302°C) by a combination of the quasi-static method of RODEBUSH and DIXON and a boiling point technique. The data are consistent with the extrapolation of the effusion measurements by RYON and TWICHELL on solid UF_4. The vapour pressures of the liquid can be represented by the equation:

$$\log P_{(\text{mm Hg})} = -\frac{16{,}840 \pm 44}{T} - 7{\cdot}549 \log T + 37{\cdot}036 \pm 0{\cdot}03$$

Extrapolation of the data to the normal boiling point of 1729°K, with the assumption of a ΔCp of vaporization of −15 cal/deg mole, gives a heat of vaporization of 51·2 ± 0·2 kcal/mole at the boiling point. The entropy of vaporization at the normal boiling temperature is 29·7 e.u. in reasonable agreement with those of other heavy metal tetrafluorides.

The close agreement between the extrapolated effusion measurements (assuming the vapour species to be monomeric) and the total pressures measured in the present study indicates the absence of associated molecules in the vapour phase.

THE vapour pressure of uranium tetrafluoride was studied in 1947 by other investigators[1,2] in connexion with its possible use in the electromagnetic isotope separation process. The data were not in agreement within the precision expected from vapour pressure measurements.

The present study was undertaken in 1954 in connexion with the use of UF_4 mixtures as fuels for the Aircraft Reactor Experiment[3] but publication has been delayed until time permitted more precise measurements to be made.

RYON and TWICHELL[1] measured the vapour pressure of UF_4 in the temperature range 740–860°C using an effusion technique[4] and in the range 1025–1184°C using the boiling point method.[5] The intermediate range between 847 and 1002°C was studied by JOHNSSON[2] using a balanced diaphragm method.[6] The effusion and boiling point data of RYON and TWICHELL were fairly consistent but the balanced diaphragm data were higher by a factor of about three. Several measurements were also made by ALTMAN[7] using an effusion technique. They appear to be quite low.

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† Operated for the United States Atomic Energy Commission by the Union Carbide Corporation.

[1] A. D. RYON, L. P. TWICHELL, Report No. H-5. 385.2 (TL-7703), Tennessee Eastman Corporation, Oak Ridge, Tennessee (1947).
[2] K. O. JOHNSSON, Report No. Y-42 (TL-8550), Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee (1947).
[3] A. M. WEINBERG, R. C. BRIANT, *Nucl. Sci. Engng.* **2**, 797 (1957); W. R. GRIMES, D. R. CUNEO, F. F. BLANKENSHIP, G. W. KEILHOLTZ, H. F. POPPENDIEK and M. T. ROBINSON, *Fluid Fuel Reactors*, Chap. 12. Addison-Wesley, Reading, Mass. (1958).
[4] M. KNUDSEN, *Ann. Phys.* **29**, 179 (1909).
[5] W. FISCHER and O. RAHLFS, *Z. Anorg. Chem.* **205**, 1 (1932).
[6] N. W. GREGORY, UCRL Report No. BC-16, (1946).
[7] Private communication from D. ALTMAN to L. BREWER (1945); L. BREWER, L. A. BROMLEY, P. W. GILLES and N. L. LOFGREN, UCRL Report No. BC-82 (1947); M. E. MUELLER, UCRL Report No. AECD-2029 (1948).

EXPERIMENTAL

Material

The UF_4 used in these experiments was high quality material which had been prepared and purified by high temperature hydrofluorination of the oxide. X-ray diffraction and petrographic examination failed to detect the presence of UO_2 or UO_2F_2 which are the most common impurities present in commercial UF_4.

Temperature measurements and control

The temperature of the melt was measured with a platinum vs. platinum–10 per cent rhodium thermocouple which was set in a centrally located thermocouple well in the vapour pressure cell. The thermoelectric potentials were read with a Rubicon type B potentiometer. The thermocouples were calibrated against standard thermocouples calibrated by the National Bureau of Standards.

The furnace temperature was controlled by a Wheelco "Capacitrol" controller and a chromel–alumel thermocouple placed close to the furnace windings of a 5 in. diameter Hoskins pot furnace. The vapour pressure cell was set inside a large nickel cylinder to a depth of about 5 in. This served to minimize the temperature variations in the sample compartment, and the temperature could be held constant to within $\pm 0{\cdot}2$°C over long periods of time.

Temperatures of the liquid are estimated to be known to about the accuracy of the thermocouple calibration, which was ± 2°C.

Vapour pressure measurements

The vapour pressures were measured in an apparatus of the type originally designed by Fiock and Rodebush[8]. This apparatus was devised for a vapour pressure techinque[8,9] in which the flow of inert gas through the vapour pressure cell is impeded and balanced by the vapour pressure of the material under investigation. This method has been used recently by Cantor[10] and Beusman[11].

For the present studies the vapour pressure apparatus was welded of "grade A" nickel and consisted of two vertical tubes, $\frac{3}{8}$ in. o.d. with a wall thickness of 0·049 in., projecting from the top of a cylinder 2 in. in diameter and 1 in. high which contained the melt and saturated vapour. The re-entrant thermocouple well, of $\frac{1}{4}$ in. o.d. tubing extended to within $\frac{1}{8}$ in. of the bottom of the reservoir, projecting about $\frac{3}{16}$ in. below the surface of the melt. Inserts[8] in the vapour tubes to limit the cross-sectional area for diffusion of the inert gas through the tubes were made of graphite.

The cell was loaded in an inert atmosphere dry box with about 100–120 g. of UF_4. The inserts were placed into the vapour tubes and diaphragm type regulating valves were attached to the tubes (permitting the cell to be handled in air) through Swagelok fittings. The cell was then placed in the furnace and connected to the vacuum manifold; this included an inert gas (argon) supply, an absolute mercury manometer, a differential oil manometer to measure pressures differences between the vertical tubes of vapour pressure cell. The cell was outgassed by pumping at temperatures up to 800°C and was then filled with argon to a pressure greater than the anticipated vapour pressure at the experimental temperature. When thermal equilibrium had been established small amounts of inert gas were drawn through the cell from the gas reservoir which was connected to the absolute manometer. Momentary pressure differences across the vapour compartment and the return to equilibrium following successive withdrawals of gas could be followed on the differential manometer. When the inert gas pressure became equal to the vapour pressure of UF_4, the diffusion of inert gas through the cell was impeded by the UF_4 vapour and a permanent difference was observable on the differential manometer. The vapour pressure of UF_4 was then obtained by reading the inert gas pressure on the manometer.

At higher pressures the increased flow of inert gas through the cell tended to lower the temperature of the melt. The advantage of converting to boiling point measurements for high pressures in this type of apparatus had been noted by Cantor[12]. Therefore, above 30 mm Hg an isothermal boiling point method was adopted for convenience as well as reliability.

The system was converted to a boiling point apparatus by merely opening both sides of the cell to the vacuum manifold. The manifold was then connected to the vacuum pump through a stopcock

[8] E. F. Fiock and W. H. Rodebush, *J. Amer. Chem. Soc.* **48**, 2522 (1926).
[9] W. H. Rodebush and A. L. Dixon, *Phys. Rev.* **26**, 851 (1925).
[10] S. Cantor, R. F. Newton, W. R. Grimes and F. F. Blankenship, *J. Phys. Chem.* **62**, 96 (1958).
[11] C. C. Beusman, Thesis University of Cincinnati (1957); Report No. ORNL-2323 (1957).
[12] S. Cantor, in preparation (1959).

and a short piece of 1 mm i.d. capillary tubing. On opening the stopcock the inert gas pressure in the system was reduced very slowly until boiling occurred. The temperature of the melt was observed continuously by keeping the galvanometer key on the potentiometer depressed. The temperature remained steady as long as the inert gas pressure was greater than the vapour pressure. But when the gas pressure was reduced to the vapour pressure, there was a sharp drop in the temperature of the liquid UF_4 and the galvanometer deflected several inches very suddenly. The stopcock was quickly closed and the pressure was read on the manometer.

RESULTS AND DISCUSSION

In this study, measurements were made from 1018–1302°C. The data obtained for the vapour pressure of uranium tetrafluoride are given in Table 1. The observed

TABLE 1.—VAPOUR PRESSURE OF URANIUM TETRAFLUORIDE

Temperature (°C)	Pressure (mm Hg)		
	Observed	Calculated	$P_{Obs.}-P_{Calc.}$
1018	3·78	3·49	0·29
1020	3·93	3·64	0·29
1029	4·68	4·44	0·24
1041	5·46	5·35	0·11
1049	6·27	6·10	0·17
1076	9·45	9·48	−0·03
1088	11·50	11·36	0·14
1107	14·91	15·14	−0·23
1130	20·60	21·18	−0·58
1159	31·61	31·77	−0·16
1171	37·43	37·36	0·07
1197	51·90	52·50	−0·60
1208	60·22	60·31	−0·14
1221	72·15	70·96	1·19
1229	77.12	78·28	−1·16
1236	87·16	85·20	1·96
1252	103·8	103·0	0·8
1261	112·2	114·4	−2·2
1265	122·0	119·8	2·2
1279	142·8	140·4	2·4
1284	152·3	148·5	3·8
1302	180·0	181·0	−1·0

* $P_{Calc.}$ is obtained from equation (1) using the constants for the liquid in Table 2 except for the three temperatures below the melting point.

pressures are the averages of at least two measurements at each temperature. The logarithms of the pressures are plotted vs. the reciprocal of the absolute temperature in Fig. 1. The effusion data on solid UF_4, obtained by RYON and TWICHELL[1] are also plotted.

The effusion data of RYON and TWICHELL show some scatter, but linear extrapolation to the melting point of UF_4 at 1036°C yields a vapour pressure in good agreement with that obtained from the present study. This is somewhat fortuitous in view of the linear extrapolation over a temperature range of 200°C.

The data of JOHNSSON[2], obtained by the balanced diaphragm technique, are

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high by a factor of three. This discrepancy may have resulted from the evolution of residual gases from the UF_4 in the diaphragm apparatus at high temperatures. ALTMAN's data[7] were obviously low and were not treated further.

The boiling point data of RYON and TWICHELL at pressures above 15 mm Hg where boiling point methods become reliable are in quite good agreement with the

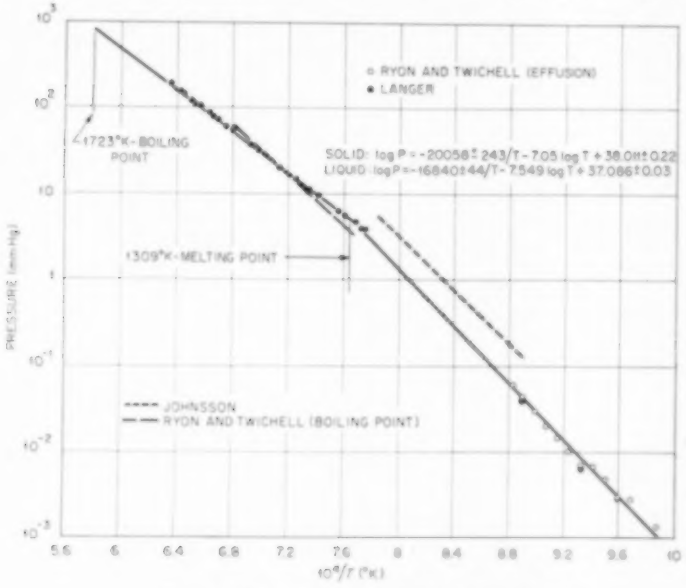
RYON AND TWICHELL (EFFUSION)
LANGER
1723°K - BOILING POINT
SOLID: log P = -20058±243/T - 7.05 log T + 38.0H±0.22
LIQUID: log P = -16840±44/T - 7.549 log T + 37.086±0.03
1309°K - MELTING POINT
JOHNSSON
RYON AND TWICHELL (BOILING POINT)
PRESSURE (mm Hg)
10⁴/T (°K)

FIG. 1.—Vapour pressure of uranium tetrafluoride.

data obtained in this study. Their results at lower pressures, however, appear low and greatly increase the slope of their least squares line (to about 65 kcal/mole). In fact, if their points below 15 mm Hg are ignored, the remaining points yield a least squares line almost coincident with that obtained by the present authors. The least square lines for the data of JOHNSSON and the boiling point data of RYON and TWICHELL are shown as broken lines in Fig. 1.

While the vapour pressure of UF_4 appears to be linear over the temperature range studied, it is not expected to be so over longer ranges. Therefore, in order to improve the extrapolation of the liquid data to the boiling point and extrapolation of the effusion data to the melting point, heat capacity corrections were applied to both sets of data. BREWER and SEARCY[13] have discussed the errors which can result from the failure to make such corrections. For the data in the liquid range, obtained in this study, a value of -15 cal/deg mole for ΔC_p of vaporization was assumed in the absence of any experimental heat capacity data. This value was based on GLASSNER's estimate[14] of the heat capacity of the liquid (41 cal/deg mole) and the classical value of the heat capacity of the gas (26 cal/deg mole).*

* Dr. GLASSNER in a private communication to the authors has stated that the last seven columns in Table 3, in ANL-5750 are in error by two lines. The data for UF_3 solid and liquid was omitted due to a printing error and all subsequent lines were raised two spaces. Thus, the data given for solid UF_3 ($a = 25{\cdot}3$, $b = 8{\cdot}0$, $A = 7{\cdot}899$, $B = 109{\cdot}6$) actually apply to solid UF_4.

[13] L. BREWER and A. W. SEARCY, *J. Chem. Educ.* **26**, 548 (1949).
[14] A. GLASSNER, Report No. ANL-5750 (1957).

The effusion data on solid UF_4, obtained by RYON and TWICHELL[1] were combined with the three measurements of this study below the melting point (see Table 1) and −14 cal/deg mole was assumed for ΔC_p of sublimation. This value was based on the ideal heat capacity of the gas and an average value of 40 cal/deg mole for the heat capacity of the solid in the range 740°–1030°C, obtained from the data of POWERS and BLALOCK.[15]

The two sets of experimental data were fitted to the equation

$$\log P\,(\text{mm Hg}) = -\frac{\Delta H_0}{2{\cdot}303RT} + \frac{\Delta C_p}{R}\log T + \frac{I}{2{\cdot}303R} \qquad (1)$$

by the method of least squares and the constants ΔH_0 and I were evaluated and are given in Table 2. These constants are in fair agreement with BREWER's estimates[16] based on ALTMAN's data.[7]

TABLE 2.—CONSTANTS IN THE FREE ENERGY EQUATIONS

Condensed phase	ΔH_0 (cal/mole)	I
Solid	91,800 ± 1100*	173·94 ± 1·0*
Liquid	77,060 ± 201*	169·70 ± 0·14*

* Standard deviation.

The normal boiling point was calculated to be 1723°K and the heat and entropy of vaporization at the normal boiling point are 51·2 kcal/mole and 29·7 e.u., respectively. An approximation for the heat of fusion, 16·1 kcal/mole, obtained from the heats of vaporization and sublimation at the melting point appears somewhat high but is not greatly different than the calorimetric value of 14·7 kcal/mole for ZrF_4 measured by POWERS.[17]

The close agreement between the extrapolated effusion measurements (assuming the vapour species to be monomeric) and total pressures measured in the present study indicates the absence of associated molecules in the vapour phase. This conclusion is substantiated by the mass spectrometric investigation of GILPATRICK *et al.*[18] who found no evidence of association in the vapour phase of UF_4.

Reasonably accurate vaporization and sublimation data are now available for the isostructural tetrafluorides in Table 3. The sublimation pressure of zirconium tetrafluoride has been studied by CANTOR[10] and the heat of fusion has been measured calorimetrically by POWERS[17]. The vapour pressures of solid and liquid thorium tetrafluoride have been studied by DARNELL and KENESHEA[19]. The heat of vaporization for ThF_4 given in Table 3 was obtained by correcting ΔH_0 of vaporization to the melting point of ThF_4 using the ΔC_p of vaporization of −19 cal/deg mole assumed by DARNELL and KENESHEA. For solid ThF_4, DARNELL and KENESHEA do

[15] W. D. POWERS and G. BLALOCK, Report No. ORNL-CF-51-11-195 (1951).
[16] L. BREWER, L. A. BROMLEY, P. W. GILLES and N. L. LOFGREN, Report No. BC-82 (1947), also quoted in F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE, NBS Circ. No. 500 (1952).
[17] Reference (8) of paper by S. CANTOR, R. F. NEWTON, W. R. GRIMES and F. F. BLANKENSHIP, *J. Phys. Chem.* **62**, 96 (1958).
[18] L. O. GILPATRICK, R. BALDOCK, J. R. SITES, Report No. ORNL-1376 (1952). (Includes data on UF_4).
[19] A. J. DARNELL and F. J. KENESHEA, *J. Phys. Chem.* **62**, 1143 (1958).

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not give a free energy equation. Their vapour pressure data were fitted to equation (1) by the present authors assuming ΔC_p of sublimation to be -18 cal/deg mole. The heat of sublimation at the melting point was obtained from this equation.

TABLE 3.—VAPORIZATION AND SUBLIMATION DATA OF THE TETRAFLUORIDES*

	Melting point (°K)	Heat of sublimation at m.p. (kcal/mole)	Heat of vaporization at m.p. (kcal/mole)	Heat of fusion (kcal/mole)	Entropy of fusion (e.u.)	Boiling point (°K)	Entropy of vaporization at normal boiling point	Pauling ionic radius (Å)
ZrF_4	1185	$52{\cdot}0 \pm 0{\cdot}5$	(37·3)	14·7	12·4	1176	31·4	0·80
UF_4	1309[1,20]	$73{\cdot}5 \pm 1{\cdot}1$	$57{\cdot}4 \pm 0{\cdot}2$	(16·1)	12·3	1723	29·7	0·97
ThF_4	1383	$73{\cdot}3 \pm 1{\cdot}3$	$72{\cdot}4 \pm 1{\cdot}5$†	(0·9)†	(0·65)†	1953	31·5	1·02

* The enthalpies given in parentheses are obtained from the other two which are experimental values.
† See text.

Since all three substances have the same crystal structure the vaporization process should reflect primarily the difference in cation size. ZrF_4 is more volatile because of better shielding of the smaller cation,[21] while UF_4 and ThF_4 are closely similar.

The entropies of vaporization at the normal boiling points are in reasonable agreement. The enthalpies for the vaporization and fusion processes are in the normal range with the exception that the heat of fusion for ThF_4 appears too low. If the heat of sublimation of ThF_4 is accepted because of its similarity to that of UF_4 then it appears that the calculated heat of fusion for ThF_4 is low because the heat of vaporization is too high. An extension of the range of vapour pressure measurements (17 mm Hg) on liquid ThF_4 would be of interest in this connexion.

Alternatively, if one assumes that the entropy of fusion is approximately the same for both UF_4 and ThF_4, then the heat of fusion of ThF_4 becomes 17 kcal/mole. Combining this heat of fusion with the measured heat of sublimation gives 56 kcal/mole as a plausible value for the heat of vaporization at the melting point.*

Acknowledgements—The authors wish to thank Dr. S. CANTOR and Dr. R. F. NEWTON for helpful suggestions and fruitful discussions.

* The authors would like to thank the referee of the paper for pointing out this approach.

[20] C. J. BARTON, R. J. SHEIL, ORNL, unpublished data. Error estimated at ± 2°C.
[21] E. A. VAN ARKEL, *Molecules and Crystals* pp. 47, 48. Interscience, New York (1949).

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COPPER(0) PHTHALOCYANINE*

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Abstract—The reduction of copper(II) phthalocyanine with potassium in liquid ammonia has been shown to yield an anionic phthalocyanine complex of copper in the zero oxidation state. Evidence is presented for the possible intermediation of copper(I) phthalocyanine and its disproportionation.

SINCE stable compounds of copper in the zero oxidation state were apparently not known,[1] the phthalocyanine ligand appeared to offer considerable promise of stabilization of Cu(0) through co-ordination. The remarkable stability of phthalocyanine complexes of divalent metal ions is well known;[2] of these the copper(II) compound is one of the most stable. This is attributable in part to the fact that the covalent radius of copper in square planar complexes is 1·32 Å as compared with the 1·35 Å gap in the centre of the phthalocyanine ligand.[3] Although the corresponding copper(0) complex might be expected to exhibit appreciable stability, it seems unlikely that such a product would be sufficiently stable to resist demetalization upon treatment with strong acids. As shown by the data given below, however, copper(0) phthalocyanine is sufficiently stable to permit sublimation at 500°.

EXPERIMENTAL

Equipment and procedures employed in this work were the same as those described previously.[4]

Pure samples of copper(II) phthalocyanine and the free unmetallated ligand were generously provided by the Pigments Department, E. I. du Pont de Nemours and Co. and were used without further purification. X-ray diffraction data for both compounds are given in Table 1. The copper(II) compound was found to have $\mu_{eff} = 1{\cdot}73$ B. M.

Preliminary experiments

The solubility of copper(II) phthalocyanine in anhydrous liquid ammonia at −33·5° was found to be approximately 20 mg/100 ml of solution.

When ca. 2·5 g of copper(II) phthalocyanine was slurried in 100 ml of ammonia at −33·5° and treated dropwise with an excess of potassium (0·51 g) dissolved in 20 ml of ammonia, the potassium was consumed rapidly, there was no gas evolution, and the vivid blue colour of the phthalocyanine changed momentarily to an intense green. Although this green colour was transitory, it became evident as the reaction progressed that the green solid reacted spontaneously to form a deep purple solid. Upon completion of the addition of potassium solution, the purple solid was separated by filtration, washed twice with 50 ml portions of ammonia, and removed from the reactor in a dry helium atmosphere. When samples of this product were exposed to the atmosphere or treated with water, the colour changed from purple to blue. The blue solid was filtered, washed with water and dried at 110°; the X-ray diffraction pattern for this solid was identical with that of copper(II) phthalocyanine (Table 1).

With a view to determining whether copper(II) phthalocyanine is reduced via a stepwise two-electron reaction, the reduction of 0·0999 g (0·1735 mmole) of the copper(II) compound in ca. 75 ml

* This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

[1] J. CHATT, *J. Inorg. Nucl. Chem.* **8**, 515 (1958).
[2] H. DE DIESBACH and E. VAN der WEID, *Helv. Chim. Acta* **10**, 886 (1927).
[3] For numerous references to studies on the structure of the phthalocyanines see: J. C. BAILAR, JR., *Chemistry of the Co-ordination Compounds* p. 760. Reinhold, New York (1956).
[4] G. W. WATT *et al.*, *J. Amer. Chem. Soc.* **70**, 1197 (1948); **71**, 3833 (1949); **76**, 4742 (1954); **79**, 3315 (1957); **79**, 5163 (1957). *J. Electrochem. Soc.* **98**, 1 (1951); **102**, 46, 545 (1955).

of ammonia by 0·0219 g (0·560 mmole) of potassium in 29 ml of ammonia at −33·5° was followed potentiometrically over a period of 42 hr. Probably because of the very limited solubility of the copper(II) compound, together with the possible disproportionation of an intermediate product

TABLE 1.—X-RAY DIFFRACTION DATA FOR PHTHALOCYANINE AND RELATED SPECIES

Phthalocyanine		$[Cu^{II}(PC)]$*		$K_2[Cu^0(PC)]\cdot 4NH_3$	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
12·76	1·0	12·62	1·0	12·34	1·0
9·93	1·0	9·65	1·0	7·77	0·7
4·94	0·5	4·81	0·4†	5·60	0·3
3·76	0·8	3·74	0·7	4·91	0·3
3·42	0·8	3·39	0·6	3·80	0·3†
2·97	0·4†	2·94	0·5	3·02	0·5

* PC = phthalocyanine group.
† Less intense lines are not included here.

(*vide infra*), the potentials were somewhat erratic and re-establishment of equilibrium following addition of each 1 ml increment of potassium solution was slow. There was no detectable change in potential corresponding to the addition of one equivalent of potassium solution, but a major change occurred upon addition of exactly two equivalents. The visual observations were the same as those described above.

Reduction of $[Cu^{II}(PC)]$ *to* $K_2[Cu^0(PC)]$

Copper(II) phthalocyanine (2·4381 g) in 100 ml of ammonia was reduced, as described above, with two equivalents of potassium (0·6250 g) in 25 ml of ammonia. The resulting purple solid was washed twice with 50 ml portions of ammonia and dried at atmospheric pressure. (Found: Cu, 8·81; N, 22·8; μ_{eff}, 1·75 B.M. Calc. for $K_2[Cu\text{-}(PC)]\cdot 4NH_3$: Cu, 8·81; N, 23·5%). X-ray diffraction data are included in Table 1.

In an experiment that differed only in that the final product was dried for 2 hr at 10^{-4} mm, 1·2356 g of the copper(II) compound in 100 ml of ammonia was reduced with 0·2369 g of potassium in 25 ml of ammonia. (Found: Cu, 9·30; N, 16·4; μ_{eff}, 1·74 B.M. Calc. for $K_2[Cu^0(PC)]$: Cu, 9·72; N, 17·1%). The X-ray diffraction pattern for this product was ill-defined; the resulting d-spacings (relative intensities in parentheses) were: 12·34 (1·0), 7·84 (0·5), 5·18 (very diffuse).

Attempted separation of $K[Cu^I(PC)]$

In an effort to isolate the phthalocyanine complex of copper(I) or its degradation products, 1·6123 g of the copper(II) compound was reduced with one equivalent (0·1153 g) of potassium in 17 ml of ammonia. The solid product was treated as described above and dried at atmospheric pressure. (Found: Cu, 9·69; N, 25·8; μ_{eff}, 1·67 B.M. Calc. for $K_2[Cu^0(PC)] + [Cu^{II}(PC)]\cdot 8NH_3$: Cu, 9·30; N, 25·4%). The presence of potassium was confirmed by a qualitative test and the presence of copper(II) phthalocyanine by means of its characteristic X-ray diffraction pattern. Efforts to separate the components of this mixture by fractional sublimation under anhydrous oxygen-free conditions were unsuccessful; at 500° and 0·03 mm both the copper(II) and copper(0) compounds sublimed. The latter was collected as clusters of purple needles but X-ray diffraction data showed that these crystals were contaminated with the copper(II) compound. Some decomposition was observed during the course of the sublimation.

DISCUSSION

The data given above show that copper(0) phthalocyanine results from the reaction,

$$[Cu^{II}(PC)] + 2K^+ + 2e^- + 4NH_3 \rightarrow K_2[Cu^0(PC)]\cdot 4NH_3 \qquad (1)$$

and that the 4-ammoniate is readily deammoniated to form the unsolvated copper(0) complex. Like the inner orbital[5] copper(II) compound, the copper(0) complex has a paramagnetic moment corresponding to one unpaired electron. Presumably, the addition of two electrons via reaction (1) results in complete utilization of the 3*d* orbitals with the unpaired electron in a 4*p* orbital.[5] As shown above, the copper(0) complex is quite stable in an inert atmosphere even at elevated temperatures, but is readily reoxidized to the copper(II) compound upon exposure to even mild oxidizing conditions. Apparently, the vapour pressures of the copper(II) and copper(0) compounds are closely similar.

Although evidence for the intermediation of a copper(I) complex,

$$[Cu^{II}(PC)] + K^+ + e^- \rightarrow K[Cu^{I}(PC)] \qquad (2)$$

is by no means unequivocal, this species should be expected to have appreciable stability. It is believed that the bright green intermediate invariably observed in the reduction of copper(II) to copper(0) is indeed the copper (I) species which disproportionates rapidly

$$2K[Cu^{I}(PC)] \rightarrow K_2[Cu^{0}(PC)] + [Cu^{II}(PC)] \qquad (3)$$

The extent of ammoniation of these products is not clear. It is possible that retention of eight moles of ammonia found by analysis is a fortuitous result of the mild conditions under which these products were dried. Nevertheless, complete deammoniation yields a product that corresponds analytically to an equimolar mixture of the copper(0) and copper(II) compounds and which has the paramagnetic moment anticipated on this basis.

Finally, it is of interest to note that SHIGEMITSU[6] has reported recently that copper(II) phthalocyanine is unreactive toward reducing agents.

[5] P. RÂY and D. N. SEN, *J. Indian Chem. Soc.* **25**, 473 (1948).
[6] M. SHIGEMITSU, *Bull. Chem. Soc. Japan* **32**, 502 (1959).

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REACTIONS OF PHOSPHINE WITH TRIMETHYLINDIUM

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Abstract—Trimethylindium reacts with phosphine at its boiling point to form a 1 : 1 adduct, which decomposes on warming to −78°C into the starting materials (75 per cent) and the compound [—MeIn—PH—]$_x$ (25 per cent). The latter material is also formed quantitatively when phosphine gas is bubbled through a solution of trimethylindium in benzene at 0–23°C. The compound decomposes sometimes explosively into indium phosphide and methane when heated to 270–300°C in inert atmospheres or *in vacuo*. No evidence for the existence of $(Me_2In—PH_2)_n$ has been found.

THE co-ordination complexes of trimethylindium with ammonia, trimethylamine, trimethylphosphine and several others have been investigated by COATES and WHITCOMBE.[1] There are no data in the literature concerning similar compounds with phosphine. The present paper is intended to fill partially this gap in the systematic chemistry of organometallic compounds.

The reaction between trimethylindium and phosphine was studied *in vacuo* and in solution. When phosphine gas is bubbled through a solution of $InMe_3$ in dry benzene, a pale yellow, flocculent precipitate appears in the course of an exothermic reaction. If the reaction temperature is kept around 0°C, the precipitate becomes more grainy with time but does not change in colour. If the temperature is allowed to rise to around 40–50°C the precipitate becomes yellow, turning orange at the boiling point of benzene.

The reaction is quantitative. The precipitate can be filtered and kept *in vacuo* or in inert atmosphere. When exposed to air it rapidly oxidizes, sometimes with conflagration. The material is insoluble in all common organic solvents. Water and acids attack it with the evolution of methane and phosphine. The product darkens progressively when it is heated in an inert atmosphere. At around 100–120°C the material has a tendency to puff or even explode violently, depending on the amount present and on the heating rate. The dark gray powder remaining after heating to 250–270°C is indium phosphide.

The thermal decomposition of this compound has been followed quantitatively in a vacuum apparatus. It has been established that for one mole of the residual indium phosphide, there is always evolved one mole of methane containing a trace of hydrogen. The mass balance proves that no other species are formed. The compound has, therefore, the empirical composition $InPCH_4$. The X-ray powder diagram showed that the material is amorphous. This, together with its insolubility, would lead one to eliminate possible cyclic di- and trimeric structures and to assume that the material is highly polymeric $(—MeIn—PH—)_n$.

COATES and WHITCOMBE[1] found that trimethylindium forms with ammonia a 1 : 1 adduct melting at 66·2–66·4°C. This compound evolves methane slowly at

[1] G. E. COATES and R. A. WHITCOMBE, *J. Chem. Soc.* 3351 (1956).

room temperature and rapidly at 70–80°C with the formation of $(Me_2In—NH_2)_x$ (m.p. 120–125°C) which decomposes on further heating to unidentified products. In view of the fact that in the case of phosphine, the last member of the series

$$Me_3In{\cdot}PH_3 \xrightarrow{-CH_4} (Me_2In—PH_2)_x \xrightarrow{-CH_4} (—MeIn—PH—)_n$$

is easily prepared by the above method, it was interesting to see if the preceding two compounds of this series do exist.

Trimethylindium is very soluble in liquid phosphine (to the extent of about 0·25 g/ml). When the liquid phosphine is distilled off at −123°C from such a solution by conventional vacuum techniques, not all of it is recovered and the amount of phosphine retained corresponds to a 1 : 1 adduct. The equilibrium pressure of phosphine over the adduct at −123°C is 4 mm Hg and 7 mm Hg at −112°C. Up to −78°C only traces of methane are formed. Above this temperature the evolution of phosphine stops, methane begins to form and continues to evolve until about 0°C. At this temperature, the original adduct is approximately 75 per cent decomposed into trimethylindium and a pale yellow non-volatile solid. The amount of methane formed up to this point corresponds to two moles of gas per mole of trimethylindium that entered the reaction to form the pale yellow solid. This material evolves only very little methane on further heating, but its colour becomes progressively darker. At 95°C it is brick-red and a fast evolution of methane begins and continues to 275–300°C. The amount of methane evolved in this stage is exactly one half of the volume formed up to 0°C. The solid residue analyses as indium phosphide. The molar ratio of indium phosphide to the total methane formed is 1 : 3.

These results lead to the following conclusions: The compound $Me_3In—PH_3$ is formed at −123°C but is unstable above that temperature. It decomposes into Me_3In and PH_3 slowly and reversibly at −112°C, rapidly at −78°C. Around this temperature the condensation of the monomeric molecules of the adduct begins. It progresses with the evolution of methane and the formation of $(—MeIn—PH—)_n$ which is completed between 0°C and 25°C. This compound is moderately stable up to about 95°C. Between this temperature and 275°C it breaks down into indium phosphide and methane. No evidence for the existence of $(Me_2In—PH_2)_x$ could be found.

In comparing these results with the work of COATES and WHITCOMBE[1], one finds the usual reduced stability of phosphine coordination compounds relative to those of ammonia, alkylamines and alkylphosphines. The fact that no phosphine analogue of $(Me_2In—PH_2)_n$ seems to exist, but a highly polymeric $(—MeIn—PH—)_n$ readily forms, is also in agreement with the growing inertness of the lone electron-pair as one progresses to higher members of a periodic group, leading to the decreasing stability of the "onium" type compounds.

EXPERIMENTAL

Trimethylindium. This compound was prepared by the method of DENNIS *et al.*[2] and purified by sublimation *in vacuo*.

Phosphine. The phosphine used was 99·9+ per cent pure, procured as compressed gas from Rocky Mountain Laboratories, Denver, Colorado.

The reaction between $In(CH_3)_3$ and PH_3 in benzene was carried out in the apparatus shown on Fig. 1. The trimethylindium was sublimed from the storage flask *A* (at room temperature) into the

[2] L. M. DENNIS, R. W. WORK and E. G. ROCHOW, *J. Amer. Chem. Soc.* **56**, 1047 (1934).

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reaction flask *B* (at −78°C). The sublimation was speeded up considerably by pumping through 1 while leaking purified argon through 2. The amount of trimethylindium sublimed into flask *B* was determined by weighing flask *A* before and after the sublimation. Benzene dried with CaH_2, was then distilled *in vacuo* through 3 into the flask *B* kept again at −78°C. After warming up to room temperature, a clear solution was formed. The apparatus was then filled with pure argon and after purging

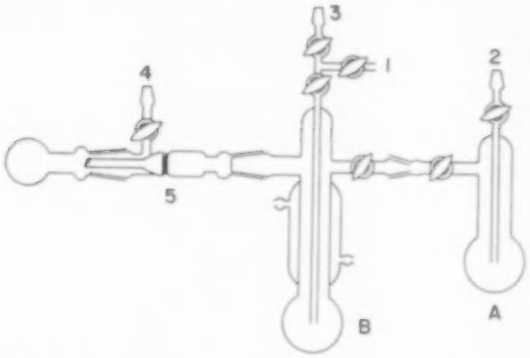

FIG. 1.—Apparatus for reacting $In(CH_3)_3$ with PH_3 in benzene.

all the external lines with PH_3 through 1 the gas was allowed to bubble through the solution. It escaped through 4 and through a mercury seal-off trap. It is best disposed of by burning and scrubbing the fumes with running water.

The precipitation at room temperature is rapid and exothermic. If the solution is concentrated in trimethylindium, it will warm up to the boiling point of benzene. After the reaction is completed, the solution and the apparatus are purged with argon entering through 1 and the precipitate is filtered through the medium porosity *fritted* glass plate 5 by tilting the apparatus and applying slight vacuum at 4 while maintaining the argon flow through 1. The filtered and vacuum dried yellow precipitate is then transferred in an inert atmosphere box into a storage flask. The reaction is quantitative.

Thermal decomposition of —(CH_3In—PH)—$_x$ *in vacuo*. The compound obtained in the above manner (0·2031 g = 1·27 mmoles) was put into a small vial, stoppered by a plug of glass wool and heated inside a tube attached to the vacuum chain. Slow gas evolution began at 95°C and proceeded rapidly at 105°C. The evolved gas was intermittently pumped through a liquid nitrogen trap into a calibrated volume by means of a Toepler pump. After heating the sample to 270°C the gas evolution stopped. The total volume of gas evolved was 26·8 ml, reduced to standard conditions, which corresponds to 1·20 mmoles. Analysis by gas chromatography showed the gas to be methane with a trace of hydrogen (<1 per cent). The remaining powder analysed as InP and weighed 0·1792 g, corresponding to 1·23 mmoles.

Formation of $(CH_3)_3$In—PH_3. Trimethylindium (0·0760 g = 0·48 mmole) was sublimed *in vacuo* into the bottom of a small tube and 401·5 ml of phosphine gas was condensed onto it at −196°C. The excess phosphine was then slowly distilled back into the calibrated volume, keeping the reactants first at about −130°C then at −123°C. At the latter temperature the equilibrium vapour pressure of phosphine over the solid residue was 4 mm while if any liquid phosphine (b.p. −87·5°C) was still present, it would have been 64 mm. The amount of phosphine recovered up to this point was 390·2 ml which means that 11·3 ml or 0·50 mmole reacted with 0·48 mmole of $In(CH_3)_3$. Upon heating to −78°C, 9·85 ml of PH_3 were evolved. On further heating to room temperature small amounts of phosphine and 4·63 ml (= 0·21 mmole) of methane were collected. Trimethylindium formed by the partial decomposition of the 1 : 1 adduct was sublimed at this point into a trap and its weight determined to be 0·0583 g. This means that the nonvolatile material contained 0·0177 g (= 0·11 mmole) of $In(CH_3)_3$, and that for each mole of the undissociated adduct 2 moles of methane were evolved with the formation of (—MeIn—PH—)$_x$. This material upon heating to 300°C evolved 2·3 ml (~ 0·10 mmole) of methane. The residue analysed as InP and weighed 0·0168 g (= 0·12 mmole).

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THE PRECIPITATION OF RUTHENIUM FROM NITRATE SOLUTIONS WITH INORGANIC AND ORGANIC SULPHIDES

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Abstract—Certain organic sulphur compounds, such as β-mercaptopropionic acid and 2-3 dimercaptopropanol-1 (BAL), have been found to be very effective reagents for precipitating ruthenium from nitric acid solution. The presence in the organic molecule of one or more —SH groups is essential. With trace concentrations of ruthenium, precipitation is aided by co-precipitation of a macro concentration of a heavy metal such as silver (I), copper (II), mercury (II) or molybdenum (III). Although the reaction resembles in many respects, including the effect of pertinent variables, the precipitation of ruthenium with hydrogen sulphide, the precipitation is not due to the formation of sulphide ion but rather to the formation of a very sparingly soluble compound with the organic reagent. Uranium, plutonium and most fission products other than ruthenium are not precipitated.

THE chemistry of ruthenium in nitric solution is in many ways different from that in other media and possessed of a singular "stubbornness", presumably due to the formation and inertness of stable nitrato nitrosyl ruthenium complexes. Thus, ruthenium(III) and (IV) form a series of stable coloured phenanthroline and dipyridine complexes in hydrochloric acid solution. Ruthenium is also readily and quantitatively reduced to the metal by treating a hydrochloric acid solution with zinc. In nitric acid solution, however, these reactions do not occur or occur very incompletely, even in the presence of nitrite suppressors such as urea or sulphamic acid. Ruthenium can be removed from nitrate solutions by oxidation to the tetroxide or by precipitation as the sulphide. BENWELL *et al.*[1] studied the chemistry of ruthenium in solutions prepared by dissolving ruthenium–nickel or ruthenium–uranium alloys in nitric acid and found that the ruthenium was precipitated from such solutions by hydrogen sulphide. The removal was improved and a more easily handled precipitate obtained by the simultaneous precipitation of copper sulphide or some other heavy metal sulphide. MILES and MARTIN[2] at Harwell investigated the copper(II) sulphide scavenging of radio-ruthenium from nitric acid solutions of irradiated uranium. These workers concluded that the mechanism of copper(II) sulphide scavenging involved conversion of ruthenium nitroso nitrate to colloidal ruthenium nitroso sulphide followed by adsorption of the colloid on particles of the copper sulphide precipitate. These results were also confirmed in our laboratory.

Although the ruthenium precipitation with hydrogen sulphide is convenient and quantitative, it suffers from several deficiencies. At acidities greater than about 0·5 M or at elevated temperatures a vigorous exothermic reaction between sulphide and nitric acid may occur. This is accompanied by the production of a gummy

[1] M. R. W. BENWELL, F. M. LEVER and A. R. POWELL, Report AERE-X/R-499 (1) (1950).
[2] G. L. MILES and F. S. MARTIN, Report AERE-C/R-412 (1950).

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precipitate of elemental sulphur. Intense radiation fields were also observed to cause some decomposition of the sulphide precipitate, resulting in incomplete ruthenium removal. The possible application of several organic sulphides as ruthenium precipitants was accordingly investigated in the hope of avoiding these difficulties.

DISCUSSION AND RESULTS

Ruthenium precipitation with copper sulphide

A series of experiments was performed in which ruthenium was precipitated from radioactive solutions with copper(II) sulphide under essentially the conditions recommended by the British workers.[1,2] Co-formed copper sulphide was found to work better than pre-formed, and precipitation by bubbling hydrogen sulphide through the solution was more effective than addition of a soluble sulphide (such as sodium sulphide or ammonium sulphide). In a series of typical experiments, hydrogen sulphide was bubbled at room temperature (ca. 25°C) for 2 hr through uranyl nitrate–nitric acid solutions containing initially 0·025 M copper nitrate (1·6 g/l.) and spiked with a solution of dissolved reactor-irradiated uranium to a level equivalent to 2 per cent of full Hanford level. The ruthenium-bearing copper sulphide precipitates were readily dissolved for analytical purposes in excess sodium cyanide solution, and the fraction of the ruthenium precipitated was determined by radiochemical analysis of the initial solution and of the supernate after centrifugation. From solutions 1 M in uranium and 0·5 M in nitric acid, ruthenium removal averaged 99·8 per cent, corresponding to decontamination factors (D.F.) of about 500 (Ru conc. before treatment/Ru conc. after treatment).

From solutions containing one or two molar uranyl nitrate and no free nitric acid, ruthenium decontamination factors were 580 and 190 respectively. In general, increase in acidity or in uranium concentration decreased ruthenium removal somewhat, and at high nitrate concentrations and/or higher temperatures there was a tendency for oxidation of hydrogen sulphide to free sulphur. The precipitation of copper sulphide was essentially complete within several minutes after the passage of hydrogen sulphide commenced. That of ruthenium was much slower, however, as shown in Table 1.

TABLE 1.—RATE OF RUTHENIUM PRECIPITATION ON CO-FORMED COPPER SULPHIDE

Time of passage of H_2S	Initial Ru remaining(%)	Ru D.F.
5 min	7·3	14
15 min	2·2	45
30 min	0·87	115
1 hr	0·36	280
2 hr	0·17	600

On prolonged passage of hydrogen sulphide, there was some reduction of uranium(VI) to uranium(IV) and of plutonium(IV) to plutonium(III); however, there was no detectable precipitation of any of these species. Similar results and decontamination factors as high as 770 were obtained with full level dissolver solutions.

Ruthenium precipitation with organic sulphur compounds

Preliminary cold experiments showed that 0·1 gm/l. ruthenium was precipitated more or less completely from nitric acid–uranyl nitrate solutions by the addition of a small concentration of 2,3-dimercaptopropanol-1 (commonly known as British Anti-Lewisite and abbreviated BAL). A number of other commercially available organic sulphur compounds were also tested. These included ethyl sulphide, ethyl disulphide, di-*p*-tolyl disulphide, α-mercapto-N-2-naphthyl-acetamide, mercaptoacetic acid, 2-mercaptoethanol, β-mercaptopropionic acid, 2-mercaptobenzothiazole, β-dithiodiglycol, benzenethiol and thioacetic acid. Only those which contained —SH groups gave precipitates with inactive ruthenium or with heavy metals from inactive solution. In addition to BAL, 2-mercaptoethanol and β-mercaptopropionic acid possessed adequate solubility and gave good precipitates. The β-mercaptopropionic acid in particular gave results both in "cold" and "hot" tests that were comparable to those with BAL. However, most of the subsequent experiments were performed with the latter.

Ruthenium scavenging with BAL—effect of variables

As with hydrogen sulphide, it was necessary to co-precipitate a heavy metal in order to obtain efficient precipitation of trace concentrations of ruthenium. Coagulation of the precipitates was more rapid when the solutions were digested at 50–80°C rather than at room temperature. Silver(I), molybdenum(III), copper(II), mercury(II) and ruthenium itself were particularly effective scavengers as shown in Table 2. The solutions in this series of experiments contained 1·7 M uranyl nitrate, fission product activity equivalent to one per cent Hanford level, 0·01 M carrier and 0·025 M BAL. They were digested for 2 hr at 55°C.

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TABLE 2.—SCAVENGING OF TRACE RUTHENIUM WITH BAL-METAL PRECIPITATES

Carrier	Ruthenium D.F.
Silver(I)	600
Molybdenum(III)	500
Mercury(II)	47
Copper(II)	300
Ruthenium(II) Sulphate	1050

Colour of the precipitates, as well as failure to detect any odour of hydrogen sulphide, indicated that the precipitates represented true compounds between BAL and the metals and were not sulphides resulting from hydrolysis of the mercaptan. Chemical analysis of the silver–BAL precipitate gave a silver to BAL mole ratio of 1·9, suggesting two silvers per BAL. This would correspond to one silver ion for each of the two —SH groups in the 2,3-dimercaptopropanol-1 molecule. The very low solubility of the silver compound in the presence of a slight excess of BAL is shown by the fact 6 M hydrochloric acid did not metathesize it to silver chloride. Also, a 0·01 M excess of silver ion precipitated the BAL so completely that the pungent mercaptan odour could no longer be detected.

The effects of nitric acid and uranium concentration on ruthenium scavenging

were similar to those observed with copper sulphide, i.e., a moderate decrease with increasing concentration, with decomposition of the precipitate at very high acidities (10 M HNO_3). Uranium and plutonium were not carried. Principal difference was the ability to digest BAL containing solutions at moderately elevated temperatures (50–80°C) without decomposition. When the mercaptans were introduced into full level plant dissolver solutions, gummy decomposition products were formed which suggested that these compounds were very unstable to radiation. This effect was traced, however, to the presence of nitrite, a radiation decomposition product of nitrate. The effect was largely or completely eliminated by the addition of nitrite suppressors, at least in laboratory scale experiments. A full level solution 0·0 M in HNO_3 and 1·9 M in uranyl nitrate was made 0·01 M in $AgNO_3$, 0·1 M in nitrite suppressor (urea, sulphamic acid, or ferrous sulphamate), 0·05 M in BAL and digested 2 hr at 50–55°C. Ruthenium decontamination factors were 200, 500 and 700 respectively. These are of the same magnitude as obtained with co-formed copper sulphide.

Comparison and applications

The degree of removal of ruthenium from either macro or tracer solutions and the effects of pertinent variables are very similar with the organic and inorganic precipitants. Under optimum conditions, quantitative precipitation is readily achieved. With both, the principal limitation is the decomposition caused by high concentrations of nitric acid, intense radiation dosage, high temperatures or nitrite oxidation. The sulphide precipitants, besides being convenient and useful for analytical chemical applications, also afford a way to decontaminate reactor fuel-element solutions from ruthenium activity. Because of the above cited limitations, treatment of partially decontaminated second cycle or product streams may be more practical than treatment of the feed solution. Use of organic sulphides without a carrier followed by adsorption of the ruthenium on a silica gel column (presumably as a complex or as a colloidal precipitate) has also been demonstrated.[3] The principal disadvantage of the organic sulphides for large scale application is their current high cost.

Acknowledgements—The investigation of organo sulphur precipitants was suggested by Professor A. F. Scott and Dr. H. R. Schimdt. Mr. W. W. Schulz and Mr. R. A. Watts, Jr. collaborated in conducting some of the full level experiments. Their contributions are greatly appreciated.

[3] W. W. Schulz, R. A. Watts, Jr. and R. L. Moore, U.S. Pat. 2 796 424 (1957).

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UNCOMMON CO-ORDINATING AGENTS—I
P,P,P′,P′-TETRAETHYLETHYLENEDIPHOSPHINE*

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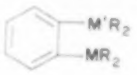
(*Received* 17 *June* 1959; *in revised form* 10 *September* 1959)

Abstract—The preparation of tetraethylethylenediphosphine (TEP) and some of its complexes is described. The complexes are compared with similar arsenic and nitrogen compounds. The ionic nature of the diamagnetic octahedral cobalt (III) complexes, $[Co(TEP)_2X_2]X$ (X = Cl, Br, I) is indicated by their conductance in nitrobenzene and in water (X = Cl). The complex $Co(TEP)_2I_2$ has one unpaired electron and, since the conductivity in nitrobenzene shows the presence of two ions, it is presumably five-co-ordinate in that solvent. It is thought to be octahedral in the solid state. A complex with the empirical formula $Co(TEP)Br_2$ is probably a salt-like dimer $[Co(TEP)_2]CoBr_4$ containing planar $[Co(TEP)_2]^{2+}$ and tetrahedral $CoBr_4^{2-}$. The complexes $M(TEP)X_2$ (M = Zn, Cd, Hg, Pb, Ni; X = Br and M = Pd, Ni; X = Cl) as well as $[M(TEP)_2](ClO_4)_2$ (M = Pb, Ni) were isolated. Those of nickel (II) are diamagnetic and presumably planar. $Ni(TEP)Br_2$ was oxidized to $Ni(TEP)Br_3$ which has one unpaired electron, confirming the presence of nickel (III). With the coinage metals, the compounds $[Cu(TEP)_2]$ $[Cu(TEP)X_2]$, $[Ag(TEP)_2]AgI_2$ and $IAuPEt_2C_2H_4PEt_2AuI$ were studied. The first two are conducting in nitrobenzene and the gold(I) complex is non-conducting. Its bridge structure is supported by its molecular weight in chloroform. It can be oxidized to $I_3Au(TEP)AuI_3$.

MANY *o*-phenylene compounds (I) in which M and M′ are arsenic, phosphorus, nitrogen or any combination of them have been prepared and the properties of their



I

co-ordination compounds investigated extensively.[1,2] In the alkyl series, the complexes of N-substituted ethylenediamines have been examined.[3] The palladium

* Taken in part from a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois, 1957, by C. E. WYMORE.

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[1] R. S. NYHOLM and G. J. SUTTON, *J. Chem. Soc.* 560 (1958) and references therein; *J. Chem. Soc.* 564, 567, 572 (1958); J. E. FERGUSSON and R. S. NYHOLM, *Chem. & Ind.* 1555 (1958); N. F. CURTIS, J. E. FERGUSSON and R. S. NYHOLM, *Chem. & Ind.* 625 (1958); H. L. NIGAM and R. S. NYHOLM, *Proc. Chem. Soc.* 321 (1958); J. CHATT and F. A. HART, *Chem. & Ind.* 1474 (1958).

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(i) F. BASOLO, *Ibid.* **75**, 227 (1953).

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complexes of alkyldiarsines(II) have also been studied.[4] Recently a preliminary report of a nickel(0) complex containing P,P,P′,P′-tetraethylethylenediphosphine* (III) has appeared.[5] This paper deals with a more extensive investigation of the metal

$$\underset{\text{II}}{R_2AsCH_2CH_2AsR_2} \qquad \underset{\text{III}}{(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2}$$

complexes of tetraethylethylenediphosphine. This diphosphine yields co-ordination compounds containing phosphorus which are similar to complexes of ethylenediamine and which can be compared with them. Tetraethylethylenediphosphine and ethylenediamine are not strictly analogous, but ethylenediamine forms stronger complexes than N-substituted ethylenediamines and trialkylphosphines form more stable complexes than phosphines, so that the chelates of these two bidentate ligands represent the most stable compounds in each series.

RESULTS AND DISCUSSION

Tetraethylethylenediphosphine. Tetraethylethlenediphosphine was prepared by the stepwise alkylation of phosphine in liquid ammonia at −78°C. None of the intermediates were isolated and the crude tetraethyldiphosphine was obtained in

$$PH_3 \xrightarrow[C_2H_5Br]{Na} C_2H_5PH_2 \xrightarrow[C_2H_5Br]{NaNH_2} (C_2H_5)_2PH \xrightarrow[ClC_2H_4Cl]{NaNH_2} (C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$$

overall yields up to 54 per cent. It was isolated and analysed as the dihydroiodide. The use of sodium amide as the base was adapted from the work of WAGNER and BURG.[6]

Trimethylenediphosphine has been prepared by LEFFLER and TEACH[7] in a similar manner. They report that ethylenediphosphine and P, P′-diethylethylenediphosphine are unstable at room temperature. HITCHCOCK and MANN[8] have prepared $(C_6H_5)C_2H_5PC_2H_4PC_2H_5(C_6H_5)$, using virtually the same method. Except for the nickel(0) compound of tetraethylethylenediphosphine, the co-ordinating ability of none of the diphosphines has been investigated.

Cobalt complexes. Tetraethylethylenediphosphine (hereafter called diphosphine and abbreviated TEP) forms complexes with cobalt(II) and (III). Air oxidation of solutions of cobalt (II) salts and the diphosphine gives a series of cobalt(III) complexes with the formula $[Co(TEP)_2X_2]X$(X = Cl, Br and I). The green bromo and chloro compounds are soluble in water and seem to hydrolyse slowly to a yellow solution. The green colour can be restored, at least in the early stages of hydrolysis, by addition of the appropriate hydrohalic acid. The brown iodo salt is insoluble in water. All three of the cobalt(III) complexes are conducting in nitrobenzene (Table 1). Their molar conductances (35–39 mhos) are a little higher than the 20–30 mhos usually found for 1 : 1 electrolytes at 20–25° in the concentration range 0·001–0·01 M[9]. The

* Can also be named ethylenebis(diethylphosphine)

[4] J. CHATT and F. G. MANN, *J. Chem. Soc.* 1622 (1939).
[5] J. CHATT and F. A. HART, *Chem. & Ind.* 1474 (1958).
[6] R. I. WAGNER and A. B. BURG, *J. Amer. Chem. Soc.* **75**, 3869 (1953).
[7] A. J. LEFFLER and E. G. TEACH, *The Preparation of Some Alkyl Diphosphines*, 133rd National A.C.S. Meeting, San Francisco, April (1958).
[8] C. H. S. HITCHCOCK and F. G. MANN, *J. Chem. Soc.* 2081 (1958).
[9] (a) A. KABESH and R. S. NYHOLM, *J. Chem. Soc.* 38 (1951);
(b) C. M. HARRIS and R. S. NYHOLM, *Ibid.* 4375 (1956).

larger values are probably due to the higher temperatures at which the measurements were made. The conductivity of the chloro complex (Table 1) in water shows that two ions are present and substantiates its uni-univalent character in nitrobenzene. All of the compounds are diamagnetic or slightly paramagnetic, indicating an octahedral configuration in which all the electrons are paired. What evidence there is (see below) might indicate that the halogen atoms are in the *trans* positions.

TABLE 1.—MOLAR CONDUCTANCE OF DIPHOSPHINE COMPLEXES

Compound	Molar conductance in $PhNO_2$			Molar conductance in H_2O	
	Temp. (°C)	Conc. ($M \times 10^{-3}$)	Λ_M	Temp. (°C)	Λ_{1024}
$[Co(TEP)_2I_2]I$	29	1·02	35·7		
$[Co(TEP)_2Br_2]Br$	28	0·79	36·9		
$[Co(TEP)_2Cl_2]Cl$	25	0·97	39·1	29	120
$[Co(TEP)_2I]I$	29	0·79	35·4		
$[Co(TEP)_2]CoBr_4$	29	0·62	16·4	26·5	233*
$Ni(TEP)Br_2$	28	0·60	3·8		
$[Cu(TEP)_2][Cu(TEP)I_2]$	28	5·60	29·4		
$[Ag(TEP)_2]AgI_2$	28	0·95	15·0		
IAu(TEP)AuI	28	1·22	0·9		
$Zn(TEP)Br_2$	28·5	1·41	0		
$Cd(TEP)Br_2$	28	5·0	0·3		

* Based on the empirical formula $Co(TEP)Br_2$.

In structure and method of preparation, the diphosphine complexes of cobalt(III), $[Co(TEP)_2X_2]X$, are similar to the analogous ethylenediamine and o-phenylenebis(dimethylarsine)[10] compounds (Formula I, M = M′ = As, R = Me). Apparently, the only previously reported complex of cobalt(III) and a phosphine is $Co(PEt_3)_2Cl_3$.[11]

The complexes of cobalt(II) are prepared in the absence of air. With a 2 : 1 ratio of diphosphine to cobalt, compounds of the empirical formulas $Co(TEP)_2I_2$ and $Co(TEP)Br_2$ were isolated. The molar conductance of the brown iodo compound in nitrobenzene is 35·4 mhos, indicating that two ions are present. This means that the cobalt is five-co-ordinate in nitrobenzene if any possible solvation by the solvent is ignored. The compound is insoluble in water so that its conductivity in that solvent could not be determined. $Co(TEP)_2I_2$ has a magnetic moment of 2·2 B.M. which indicates one unpaired electron. Both square planar and spin-paired tetragonal cobalt(II) complexes have a theoretical moment corresponding to one unpaired electron (1·73 B.M.) when calculated by the "spin only" formula, but, because of more orbital contribution the values for the square planar configuration are usually higher. The ranges of values usually found are 2·1–2·9 B.M. and

[10] F. H. BURSTALL and R. S. NYHOLM, *J. Chem. Soc.* 3570 (1952).
[11] R. G. WILKINS, *Nature, Lond.* **167**, 434 (1951).

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1·7–2·0 B.M. for four- and six-co-ordinate complexes respectively.[12] The magnetic moment for $Co(TEP)_2I_2$ is almost between the expected ranges; however, the octahedral (or tetragonal) structure is preferred for the solid state of this compound because the infrared spectra of $Co(TEP)_2I_2$ and all of the cobalt(III) compounds, $[Co(TEP)_2X_2]X$, are very similar. The individual variations in absorption frequencies among the cobalt(III) complexes are as great as the differences between each of them and the cobalt(II) iodo compound. If the five-co-ordinate cobalt compound is a square pyramid as expected, then the two diphosphine molecules are probably at the base. Such an arrangement would suggest a *trans* structure for solid $Co(TEP)_2I_2$ and probably also for the cobalt(III) complexes.

Penta-co-ordinate cobalt(II) is not unexpected for it is in accord with the crystal field theory.[13] Other cobalt(II) compounds which are probably five-co-ordinate are $Co(TAS)I_2$[14] and Co(SPA)[15] (TAS = methyl-*bis*-(3-dimethylarsinopropyl)arsine and SPA = *bis*-salicylaldehyde-γ,γ'-diaminodipropylamine). Nyholm and co-workers have shown that *o*-phenylenebis(dimethylarsine) (PDA) complexes of Pd(II)[9b,16a], Ni(II)[17], Pt(II)[17] and Au(III)[16] have conductances in nitrobenzene which support five-co-ordinate structures in that solvent. The complexes have the general formula $[M^{+n}(PDA)_2X]^{+n-1}$ (X usually halide) if any possible co-ordination by nitrobenzene is ignored. In the solid state, the $M^{II}(PDA)_2I_2$ complexes have four arsenic atoms in a plane and the two iodine atoms in a distorted octahedral arrangement.[17]

In contrast to $Co(TEP)_2I_2$, green $Co(TEP)Br_2$ has a magnetic moment of 3·7 B.M. per cobalt atom. Tetrahedral cobalt(II) complexes have a theoretical moment of 3·88 B.M. corresponding to three unpaired electrons when it is calculated by the "spin only" formula. In practice, however, the values are higher due to orbital contribution and the range usually found for tetrahedral structures is 4·3–4·8 B.M.[12] Thus the value of 3·7 B.M. for $Co(TEP)Br_2$, calculated per cobalt atom, is lower than expected for a tetrahedral arrangement. Another structure for $Co(TEP)Br_2$ is the salt-like dimer $[Co(TEP)_2]\ CoBr_4$. The observed magnetic moment would then be a mean of the magnetic moments for $[Co(TEP)_2]^{2+}$ and $CoBr_4^{2-}$. In the pyridinium salt, $CoBr_4^{2-}$ has a magnetic moment of 4·67 B.M.[18] which leaves a remainder of 2·3 B.M. for $[Co(TEP)_2]^{2+}$. This corresponds to one unpaired electron and is in the range expected (2·1–2·9 B.M.) for a square planar cobalt(II) complex.[12] It is also in line with the value of 2·2 B.M. for the one unpaired electron in six-co-ordinate $Co(TEP)_2I_2$.

The conductivity of $[Co(TEP)_2]\ CoBr_4$ in nitrobenzene is 16·4 mhos. This value is much lower than expected because 2 : 2 electrolytes should have higher conductances than the 20–30 mhos found for 1 : 1 electrolytes. The lower value may be due to a rearrangement

$$[Co(TEP)_2]CoBr_4 \rightleftarrows 2\ Co(TEP)Br_2$$

[12] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.* 12 (1954).
[13] F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* p. 59. John Wiley, New York (1958).
[14] G. A. Barclay and R. S. Nyholm, *Chem. & Ind.* 378 (1953).
[15] M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.* **68**, 2267 (1946).
[16] (a) C. M. Harris, R. S. Nyholm and N. A. Stephenson, *Rec. Trav. Chim.* **75**, 687 (1956);
(b) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.* 63 (1957).
[17] C. M. Harris, R. S. Nyholm and N. C. Stephenson, *Nature, Lond.* **177**, 1127 (1956).
[18] R. S. Nyholm, *Quart. Rev.* **7**, 377 (1953).

in nitrobenzene. Alternatively, if the compound exists as $Co(TEP)Br_2$ in the solid state, its small conductance (8·2 mhos based on the simple formula) may be due to dissociation into the ionic structure.

The molar conductance of $Co(TEP)Br_2$ in water ($\Lambda_{1024} = 233$ mhos based on the simple formula) indicates the presence of three ions per cobalt atom. Hydrolysis of either the non-ionic or ionic structure is consistent with this behaviour. The reading was taken 3 min after dissolution which liberated no diphosphine. While the evidence from magnetic and conductivity data is inconclusive, it seems to favour formulation of the complex as $[Co(TEP)_2]CoBr_4$ containing planar $[Co(TEP)_2]^{2+}$ and tetrahedral $CoBr_4^{2-}$.

Square planar complexes of cobalt(II) with *o*-phenylenebis(dimethylarsine) containing two molecules of base, $[Co(PDA)_2]X_2$, have been isolated.[19] With cobalt(II), ethylenediamine is inclined to form six-co-ordinate complexes containing three molecules of base,[20] so that diphosphine tends to resemble the diarsine chelating agent.

Both of the brown iodo cobalt complexes, $[Co(TEP)_2I_2]I$ and $Co(TEP)_2I_2$, can be changed to green by heating for long periods *in vacuo* over phosphorus(V) oxide. Traces of moisture turn the complexes brown and reheating turns them green again. Green and brown $Co(TEP)_2I_3$ give the same analysis, but $Co(TEP)_2I_2$ loses approximately 10 per cent of its diphosphine on such treatment. Too much heating converts them into blue compounds. Green $Co(TEP)_2I_2$ has a magnetic moment of 3·9 B.M. (three unpaired electrons), but enough green $Co(TEP)_2I_3$ was not available for a magnetic measurement. The infra-red spectra of these two green compounds and that of green $[Co(TEP)_2]\ CoBr_4$ are very similar. The main feature of their spectra is a quite broad absorption frequency at approximately 1100 cm^{-1}. This similarity, along with the magnetic moment of green $Co(TEP)_2I_2$, might be interpreted as suggesting a similarity in structure for all of these compounds.

Nickel complexes. Two diphosphine complexes with the formula $Ni(TEP)X_2$ (X = Cl, Br) were prepared. The chloro compound contained only one molecule of diphosphine even though a 2 : 1 ratio of diphosphine to nickel was used in its preparation. With the very poor co-ordinating anion, perchlorate, the 2 : 1 complex $[Ni(TEP)_2](ClO_4)_2$ was isolated. All of the complexes are diamagnetic, indicating a square planar structure.

Attempts to oxidize $Ni(TEP)Cl_2$ with chlorine in solution, suspension or in the solid state led to unstable or ill-defined products. Oxidation of a dilute solution of $Ni(TEP)Br_2$ in benzene by bromine gave a green-black precipitate which analysed fairly well for the empirical formula $Ni(TEP)Br_3$. The magnetic moment of this complex was 2·0 B.M., indicating one unpaired electron and confirming the presence of nickel(III). The complex was very insoluble in water, but in solvents such as ethanol, acetone and chloroform, in which it was slightly soluble, it appeared to give momentarily a green solution which then turned brown. The green colour persisted longest in nitrobenzene, in which it was essentially non-conducting. This indicates a five-co-ordinate structure, ignoring any possible co-ordination by nitrobenzene. The evidence seems to indicate a polymeric octahedral nickel(III) compound

[19] R. S. Nyholm, *J. Chem. Soc.* 2071 (1950).
[20] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, *Stability Constants, Part I: Organic Ligands* p. 5. The Chemical Society, London (1957).

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in the solid state which tends to decompose when it is dissolved, rather than a penta-co-ordinate square pyramid such as found for $Ni(PEt_3)_2Br_2$.[21]

CHATT and HART[5] have prepared $Ni(TEP)(CO)_2$, which contains nickel(0) and tetraethylethylenediphosphine. Attempts to co-ordinate two molecules of diphosphine failed. With *o*-phenylenebis(diethylphosphine) (PEP) (Formula I, M=M′=P, R = C_2H_5) a compound of analogous composition is formed, as well as a complex containing only the phenylenediphosphine, $Ni(PEP)_2$.

Complexes of nickel(II) with *o*-phenylenebis(dimethylarsine) containing one, two or three molecules of base have been isolated,[22] the one containing two molecules being most easily prepared. It is believed to be five-co-ordinate in nitrobenzene. Oxidation to nickel(III)[22] and even nickel(IV)[23] has been accomplished. Nickel(0) compounds containing one[22a] and two[5] molecules of diarsine have been prepared. Ethylenediamine and nickel(II) tend to form *tris* compounds, but this tendency is reduced with N-monoalkyl derivatives and still further decreased with N-N′-dialkylethylenediamines.[3b] A *bis* complex of N,N′-dimethylethylenediamine has been prepared,[3c] but attempts to form complexes of nickel and N,N,N′,N′-tetramethylethylenediamine were unsuccessful.[3a] In composition and ability to stabilize the different oxidation states of nickel, tetraethyldiphosphine more closely resembles the diarsines.

Coinage metal complexes. The silver(I) and copper(I) complexes isolated, $[Cu(TEP)_2][Cu(TEP)I_2]$ and $[Ag(TEP)_2]AgI_2$, are very similar. The ionic structures are assigned on the basis of the conductivities in nitrobenzene. The conductivity of the silver compound is lower than the 20–30 mhos usually found for 1 : 1 electrolytes, a property in which it resembles the analogous silver compound of *o*-diethylphosphinophenyldiethylarsine[2b] (Formula I, M = P, M′ = As, M = C_2H_5, abbreviated P–As). Copper(I) compounds of the general formula $[M(P–As)_2]A$ in which A is halogen or CuX_2^- (X = Cl,Br) as well as the silver(I) compound, in which A is iodide, have normal conductivities, but the silver complex in which A is AgI_2^- has a lower conductivity. The explanation suggested is a dissociation into a neutral three-co-ordinate species:

$$[Ag(base)_2]AgI_2 \rightleftarrows 2\ Ag(base)I$$

Attempts to resolve the compounds $[Cu(P–As)_2]I$ and $[Au(P–As)_2]I$ were not successful, but X-ray studies proved they were tetrahedral. Copper complexes of diarsines[2b,9a] have similar formulas and are thought to be tetrahedral. Copper(I) and silver(I) iodo monophosphines have a tetrameric structure $[M(PR_3)I]_4$ in which the central atoms are tetrahedral.[24]

Silver(I) and ethylenediamine (en) form the compounds $[AgH(en)]^{2+}$, $Ag(en)^+$, $Ag_2(en)^{2+}$, $Ag(en)_2^+$ as well as the dimer $Ag_2en_2^{2+}$.[25] The silver is probably linear in all of them and the ethylenediamine monodentate or bridging. Cryoscopic measurements on $[Ag_2en_2]SO_4$ support the dimeric structure which probably contains a

[21] K. A. JENSEN and B. NYGAARD, *Acta. Chem. Scand.* **3**, 474 (1949).
[22] R. S. NYHOLM, *J. Chem. Soc.* (a) 2061 (1950); (b) 2906 (1952).
[23] R. S. NYHOLM, *J. Chem. Soc.* 2602 (1951).
[24] F. G. MANN, D. PURDIE and A. F. WELLS, *J. Chem. Soc.* 1503 (1936); 1828 (1937); F. G. MANN and A. F. WELLS, *Nature, Lond.* **140**, 502 (1937); A. F. WELLS, *Z. Krist.* **94**, 447 (1936).
[25] G. SCHWARZENBACH, H. AKERMAN, B. MAISSEN and G. ANDEREGG, *Helv. Chim. Acta* **35**, 2337 (1952); P. JOB, *C. R. Acad. Sci., Paris* **176**, 442 (1923); **184**, 1066 (1927).

ten-membered ring. Copper(I) forms the compound $Cu(en)_2^+$ in which ethylenediamine is monodentate.[26] Thus, in its ability to form four-co-ordinate compounds with silver(I) and copper(I), the disphophine is similar to the diarsines.

The gold(I) complex is of a different type, having the empirical formula $Au_2(TEP)I_2$. It is almost non-conducting in nitrobenzene. Its molecular weight of 820 (ebulliscopic in chloroform) compared to the calculated 854·5 indicates that the diphosphine serves as a bridge. The gold is probably linear two-co-ordinate to give the structure IAu(TEP)AuI. The difference in behaviour of gold(I) as compared to silver(I) and copper(I) is probably due to the reluctance of gold(I) to form four-co-ordinate structures. Yet 4-methyl-*o*-phenylenebis(diethylphosphine),[2c] *o*-diethylphosphinophenyldiethylarsine[2b], and *o*-phenylenebis(dialkylarsines)[2b,16] form complexes which contain two molecules of base and are four-coordinate. These phenylene chelates have a rigid structure in which the co-ordinating atoms are held in a position favorable for chelation, while tetraethylethylenediphosphine can form a bridge more readily.

Oxidation of $Au_2(TEP)I_2$ by iodine gives a black compound of the composition $Au_2(TEP)I_6$. It is probably also bridged, with the gold(III) having a square planar structure as $I_3Au(TEP)AuI_3$. This reaction is very similar to the oxidation of gold(I) monophosphine complexes, $Au(PR_3)X$, to square planar gold(III) compounds, $Au(PR_3)X_3$.[27,28]

Oxidation of $[Au(PDA)_2]I$ produces $[Au(PDA)_2I_2]I$, which preliminary X-ray studies show to have a *trans* octahedral structure. $Au(PDA)_2(NO_3)_3$ is five-coordinate in nitrobenzene, but completely ionized in water to four-co-ordinate $[Au(PRA)_2]^{3+}$, the perchlorate of which was also isolated.[16] With ethylenediamine, gold(III) forms the complexes $[Au(en)X_2]X$ and $[Au(en)_2]X_3$[29] but these compounds were not prepared by oxidation of gold(I) complexes as are the diarsines and diphosphines. A bridging structure like that of $Au_2(TEP)I_6$ has been postulated for $(CH_3)_3AuNH_2$-$C_2H_4NH_2Au(CH_3)_3$.[30] With gold(III) it is difficult to decide whether the diphosphine compound is more similar to those of ethylenediamine or of the diarsines.

Zinc, cadmium and mercury complexes. Bromo compounds containing each of these metals with one mole of diphosphine were prepared. They are assigned the structure $M(TEP)Br_2$ on the basis of the non-conducting nature of the zinc and cadmium compounds in nitrobenzene. When cadmium bromide and diphosphine react, a complex of empirical formula $Cd_3(TEP)_2Br_6$ is first precipitated. Recrystallization of this compound from dimethylformamide by addition of water gives the simple compound $Cd(TEP)Br_2$. By dissolving one mole each of $Cd(TEP)Br_2$ and cadmium bromide in dimethylformamide and precipitating with water, followed by recrystallization in the same manner, $Cd_3(TEP)_2Br_6$ is again obtained. The ease of conversion suggests that the tricadmium compound should be formulated as a mixed crystal $2Cd(TEP)Br_2 \cdot CdBr_2$, although bridged complexes of cadmium and monophosphines are well known.[3] With similar treatment $Zn(TEP)Br_2$ did not give a compound containing greater than a 1 : 1 ratio of zinc to diphosphine. The mercury

[26] J. BJERRUM, and E. J. NIELSEN, *Acta Chem. Scand.* **2**, 307 (1948); J. E. B. RANDLES, *J. Chem. Soc.* 802 (1941).
[27] F. G. MANN and D. PURDIE, *J. Chem. Soc.* 1235 (1940).
[28] M. F. PERUTZ and O. WEISZ, *J. Chem. Soc.* 438 (1946).
[29] B. P. BLOCK and J. C. BAILAR, JR., *J. Amer. Chem. Soc.* **73**, 4722 (1951); C. S. GIBSON and W. M. COLLES, *J. Chem. Soc.* 2407 (1931).
[30] H. GILMAN and L. A. WOODS, *J. Amer. Chem. Soc.* **70**, 550 (1948).

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compound, $Hg(TEP)Br_2$, is very insoluble and could not be recrystallized from any solvent, so that the analysis is not as good as might be hoped. These compounds are probably tetrahedral like the monophosphine complexes.[31]

With ethylenediamine, zinc, cadmium and mercury tend to form compounds containing three molecules of base. With tetraethylethylenediamine the compound $Cd(base)Cl_2$ has been isolated, but it is unstable in water.[3a] Precipitation of basic substances interfered with the determination of the stability constants of zinc and dialkylethylenediamines.[3d] Evidently, no compounds of diarsines with these metals have been prepared.

Palladium complex. Reaction of ammonium tetrachloropalladate(II) or dichloro-(tetrahydrogenethylenediaminetetraacetate)palladium(II) five hydrate with a molar ratio of diphosphine gives the complex $Pd(TEP)Cl_2$. Attempts to form a compound containing two molecules of diphosphine by allowing $[Pd(NH_3)_4]Cl_2$ to react with two moles of diphosphine (charcoal catalyst) or by causing $Pd(TEP)Cl_2$ to react with more diphosphine gave only the neutral mono(diphosphine) compound. With the thought that the chloride ion was such a good co-ordinating agent that it prevented the second molecule of diphosphine from reacting, the latter reaction was repeated in the presence of silver sulphate to precipitate the chloride. This procedure led to a white solid contaminated with palladium black which on recrystallization gave more palladium metal. The product may have been unstable $[Pd(TEP)_2]SO_4$.

The colourless palladium compound is probably monomeric $Pd(TEP)Cl_2$ rather than $[Pd(TEP)_2]PdCl_4$. Although no definite proof for this was obtained, all *o*-phenylene compounds of palladium with chloride containing one mole of base are yellow or colourless, while the compounds $[Pd(base)_2]PdCl_4$, which are often intermediates, are much darker.[2a,b,d,4] It is interesting that CHATT and MANN have isolated compounds of the type $[Pd(base)_2]^{2+}$ with substituted *o*-phenylenediarsines, but under identical conditions substituted ethylenediarsines give complexes containing one molecule of base. This may again be due to the rigid structure of *o*-phenylene compounds, which makes it easier to crowd the alkyl groups around the metal.

Many of the *o*-phenylene compounds in which the co-ordinating atoms are combinations of As, N and P, as well as ethylenediamines, form complexes of the compositions $Pd(base)X_2$ and $Pd(base)_2X_2$ (X = halogen). Most of the compounds are probably four-co-ordinate planar. However the $Pd(PDA)_2X_2$ complexes are 1 : 1 electrolytes in nitrobenzene and have a tetragonal structure in the solid state. $[Pd(PDA)_2](ClO_4)_2$ is four-co-ordinate.[9b,16a] Dichloro- and dibromo-*bis*(*o*-dimethylaminophenyldiethylphosphine)palladium(II) are said to be five-co-ordinate in nitrobenzene and four-co-ordinate in water.[2d]

Preliminary attempts to prepare platinum(II) compounds of tetraethylethylenediphosphine were unsuccessful.

Lead complexes. Two compounds containing four-co-ordinate lead(II) were isolated. They were $Pb(TEP)Br_2$ and $[Pb(TEP)_2](ClO_4)_2$.

CONCLUSIONS

In general, the co-ordinating ability of tetraethylethylenediphosphine is more similar to that of *o*-phenylenebis(dimethylarsine) than that of ethylenediamine. Before a more valid comparison can be made, more information on the stability and chemical

[31] R. C. EVANS, F. G. MANN, H. S. PEISER and D. PURDIE, *J. Chem. Soc.* 1209 (1940).

reactions of the complexes is needed, particularly for the diarsines and diphosphines.

In several cases the difference between tetraethylethylenediphosphine and ethylenediamine is due to the tendency of ethylenediamine to expand the co-ordination number of a metal. With substituted ethylenediamines this tendency is reduced, but a strict comparison is not valid because the reason for complexes of lower co-ordination number for substituted ethylenediamines is due at least in part to reduced co-ordinating ability and not entirely due to steric factors. Attempts to co-ordinate ethylenediphosphine itself will be hampered by its reported instability.[7]

Probably the principal reason for the similarity of diphosphine and diarsines is the ability of both to form π-bonds. Arsenic and phosphorus atoms, but not nitrogen, have vacant *d*-orbitals so that partial double bonding can occur with metals which have electrons in their *d*-orbitals, thereby strengthening the bond. Also, the ability of diphosphines and diarsines to stabilize both lower and higher oxidation states of nickel is probably due to their ability to π-bond.[5,32]

EXPERIMENTAL

P, P, P′, P′-Tetraethylethylenediphosphine

A one litre three-necked standard taper round-bottomed flask with a side arm was fitted with an all-glass stirrer in one neck and a nitrogen inlet in another. The side arm was used as a gas outlet. The third neck of the flask was used to add solids, attach a separatory funnel or as a place for a dipstick which was used to bubble phosphine into the solution.

Air was flushed out of the system with nitrogen, which was used as a blanket throughout the experiment, and the apparatus was cooled to $-78°$ with dry ice. Approximately 600 ml of liquid ammonia was introduced and 7·22 g (0·31 mole) of sodium was dissolved in it. Dry phosphine was bubbled through the solution with stirring until the blue colour changed to light yellow. The excess phosphine was purged with nitrogen and the dipstick was removed. The small amount of white precipitate present, probably sodium hydroxide, is not harmful.

With the stirrer running, 33·9 g (0·31 mole) of ethyl bromide was added dropwise and stirring was continued for 15 min after addition was completed. If the sodium bromide which precipitated during the reaction was allowed to settle, the solution was clear. A suspension of sodium amide, freshly prepared from 8·09 g (0·35 mole; 10 per cent excess) of sodium in approximately 100 ml of liquid ammonia,[33] was added and the mixture was stirred for 1 hr. This produced a green colour. The repeat addition of ethyl bromide discharged the green colour. Addition of more sodium amide turned the mixture red-orange. After one hour's stirring, it was deep red. Then ethylenedichloride was added dropwise with stirring until the red colour was discharged. Stirring was continued for 15 min. The amount of ethylenedichloride required was 13·8 g (theor. 15·4 g, 0·155 mole). The dry-ice bath was removed and the liquid ammonia was allowed to evaporate.

Two hundred millilitres of oxygen-free water (used throughout) and 300 ml of ethyl ether were added and the mixture was stirred until all the salts had dissolved. The mixture was transferred to a separating funnel, and the water layer and dark solids (elemental iron from sodium amide preparation) were separated and washed with 75 ml of ether. The combined ether extracts were washed with three 150 ml portions of water and dried over anhydrous sodium sulphate. The ether was removed under diminished pressure; the temperature of the distilling flask was then increased to 100° for a few minutes to make sure that all excess starting materials and lower phosphines were removed. The yield of crude product was 17·5 g (54 per cent). The yellow liquid was used without further purification.

Tetraethylethylenediphosphine dihydroiodide

A solution of 1·4 ml of concentrated hydroiodic acid was added to 0·26 g (1·26 mmoles) of the crude diphosphine. The reaction mixture was evaporated almost to dryness and precipitated with absolute alcohol. The crystals were dissolved in a few drops of water and heated on a steam bath.

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Twenty-five millilitres of absolute ethanol was added dropwise and the solution was allowed to cool slowly to room temperature. Then it was cooled in an ice-bath, and the crystals which formed were collected on a filter and washed with ethanol. After two recrystallizations, the colourless crystals were dried *in vacuo* over phosphorus(V) oxide. The compound does not have a sharp melting point, but the major portion of it melts at 181–183°. (Found: C, 25·99; H, 5·85; I, 55·00. Calc. for $C_{10}H_{25}P_2I_2$: C, 25·99; H, 5·67; I, 54·93%).

Diphosphine complexes

All of the complexes were dried *in vacuo* over phosphorus(V) oxide. If the temperature used was other than room temperature, it is listed. Most of the analytical data* as well as the magnetic moments and conductivities are shown in the tables.

TABLE 2.—MAGNETIC MOMENTS OF DIPHOSPHINE COMPLEXES

Compounds	Temp. (°C)	$\mu_{eff.}$ (B.M.)
$[Co(TEP)_2I_2]I$	27·0	diamagnetic
$[Co(TEP)_2Br_2]Br$	30·0	sl. paramagnetic
$[Co(TEP)_2Cl_2]Cl$	26·5	diamagnetic
$Co(TEP)_2I_2$	29·0	2·2
$[Co(TEP)_2]CoBr_4$	29·0	3·7*
$Ni(TEP)Br_2$	27·5	diamagnetic
$Ni(TEP)Cl_2$	28·0	diamagnetic
$[Ni(TEP)_2](ClO_4)_2$	27·5	diamagnetic
$Ni(TEP)Br_2$	28·0	2·0

* Per cobalt atom.

Diiodo-bis-(diphosphine)cobalt(III), *iodide*, $[Co(TEP)_2I_2]I$. A solution of 0·34 g (1·08 mmoles) of cobalt(II) iodide in 2 ml of water and 10 ml of ethanol was added to 0·44 g (2·14 mmoles) of diphosphine in 3 ml of ethanol. The solution, which turned dark brown immediately, was shaken for 4·5 hr. It was evaporated to a small volume and cooled in an ice-bath. The $[Co(TEP)_2I_2]I$ was collected on a filter, recrystallized from absolute ethanol and dried at 50°. It is insoluble in water.

Effect of heat on diiodo-bis-(diphosphine)cobalt(III) *iodide*. A sample of $[Co(TEP)_2I_2]I$ was heated at 110° *in vacuo* for 53 hr over phosphorus(V) oxide. The sample turned green, but it did not lose diphosphine. (Found: C, 28·08; H, 5·69. Calc. for $CoC_{20}H_{50}P_4I_2$: C, 28·19; H, 5·68%).

Dibromo-bis-(diphosphine)cobalt(III) *bromide*, $[Co(TEP)_2Br_2]Br$. A solution of 0·22 g (1 mmole) of cobalt(II) bromide in 5 ml of ethanol was poured into a flask containing 0·42 g (2·04 mmoles) of diphosphine in 15 ml ethanol. The mixture was refluxed for 2 hr while air bubbled through it. After evaporation to dryness, the $[Co(TEP)_2Br_2]Br$ was recrystallized from water and dried.

Dichloro-bis-(diphosphine)cobalt(III) *chloride*, $[Co(TEP)_2Cl_2]Cl$. This compound was prepared in the same manner as $[Co(TEP)_2Br_2]Br$. One-half gramme (2·42 mmoles) of diphosphine, 0·29 g (1·22 mmoles) of cobalt(II) chloride six hydrate, and 0·21 ml of 6 N hydrochloric acid in 10 ml of ethanol were allowed to react for 1·5 hr. The yield was 0·31 g (45 per cent). $[Co(TEP)_2Cl_2]Cl$ is soluble in water, ethanol, acetone, chloroform, bromoform and nitrobenzene. It is almost insoluble in benzene and carbon tetrachloride.

Diiodo-bis-(diphosphine)cobalt(II), $Co(TEP)_2I_2$. This compound is very sensitive to oxidation so that all operations after addition of the diphosphine were carried out under a nitrogen blanket. A filtered solution of 0·15 g (1·26 mmoles) of cobalt(II) carbonate dissolved in 0·46 ml of 47 per cent hydroiodic acid and 3 ml of water was added to a boiling solution of 0·5 g (2·50 mmoles) of diphosphine in 7 ml of ethanol. Boiling water (approximately 20 ml) was slowly added until brown needles

* The microanalyses were performed by Mr. J. NEMETH, Mrs. M. BENASSI, Mr. R. NESSETT and Mrs. R. JU.

TABLE 3.—DIPHOSPHINE COMPLEXES PREPARED

Compound	Colour	Calculated			Found		
		C	H	X	C	H	X
$[Co(TEP)_2I_2]I$	dark-brown	28·19	5·68	44·68	28·22	5·99	45·11
$[Co(TEP)_2Br_2]Br$	green	33·77	6·80	33·71	34·15	7·28	33·32
$[Co(TEP)_2Cl_2]Cl$	light green	41·57	8·37	18·41	41·58	8·68	18·31
$Co(TEP)_2I_2$	brown	33·12	6·67	35·00	33·05	6·96	33·70
$[Co(TEP)_2]CoBr_4$	green	28·26	5·69	37·61	27·91	5·76	38·32
$Ni(TEP)Br_2$	red-brown	28·27	5·70	37·63	28·20	5·51	37·55
$Ni(TEP)Cl_2$	yellow-brown	35·76	7·20	21·11	35·82	7·13	21·40
$[Ni(TEP)_2](ClO_4)_2$	yellow	35·84	7·22	—	36·23	7·11	—
$Ni(TEP)Br_2$	green-black	23·80	4·79	47·50	24·04	5·45	46·12
$[Cu(TEP)_2][Cu(TEP)I_2]$	colourless	36·04	7·26	25·41	36·22	6·97	25·36
$[Ag(TEP)_2]AgI_2$	colourless	27·33	5·49	—	26·63	5·50	—
IAu(TEP)AuI	colourless	14·05	2·83	46·16*	14·27	2·91	46·33*
$I_2Au(TEP)AuI_2$	black	8·82	1·78	55·90	9·16	1·80	54·58
$Zn(TEP)Br_2$	colourless	27·84	5·61	37·04	27·87	5·60	37·23
$Cd(TEP)Br_2$	colourless	25·10	5·06	33·40	24·76	4·95	33·54
$Cd_3(TEP)_2Br_6$	colourless	19·54	3·94	—	19·97	4·37	—
$Hg(TEP)Br_2$	colourless	21·19	4·27	28·20	19·72	4·02	28·91
$Pd(TEP)Cl_2$	colourless	31·29	6·30	18·47	31·06	6·15	19·07
$Pb(TEP)Br_2$	colourless	20·95	4·22	27·88	20·73	4·53	27·22
$[Pb(TEP)_2](ClO_4)_2$	colourless	29·34	5·91	—	29·10	5·73	—

* Gold analysis.

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formed. The mixture was cooled in an ice-bath and the $Co(TEP)_2I_2$ was collected on a filter. Part of the sample was recrystallized by dissolving in ethanol and precipitating with water.

Effect of heat on diiodo-bis-(diphosphine)cobalt(II). A sample of $Co(TEP)_2I_2$ was heated *in vacuo* over phosphorus(V) oxide for 12 hr at 122° followed by 12 hr at 130°. It turned green and lost some diphosphine (~10 per cent), as indicated by the analysis and by the odour of phosphine when the apparatus was opened. The magnetic moment of the mixture is 3·9 B.M. (Diamagnetic correction based on $Co(TEP)_2I_2$.)

	Found	Calc. for $Co(TEP)_2I_2$	Calc. for $Co(TEP)I_2$
C	30·16	33·12	23·14
H	6·05	6·67	4·66

Bis-(diphosphine)cobalt(II) *tetrabromocobaltate*(II), $[Co(TEP)_2]CoBr_4$. To 0·25 g (1·14 mmoles) of cobalt(II) bromide in 3 ml of hot absolute ethanol was added a solution of 0·43 g (2·08 mmoles) of diphosphine in 2 ml of the same solvent. The blue solution turned green, and on standing a green precipitate formed. After cooling in an ice-bath, the product was collected on a filter. When recrystallized from isopropyl alcohol, it became sticky, but it dried out at 50° to a green solid. $[Co(TEP)_2]CoBr_4$ is soluble in water, methanol, ethanol, chloroform and acetone.

Dibromodiphosphinenickel(II), $Ni(TEP)Br_2$. A hot solution of 0·38 g (1·74 mmoles) of nickel(II) bromide in 4 ml of absolute ethanol was added to 0·36 g (1·74 mmoles) of diphosphine in 2 ml of

absolute ethanol. Brown crystals formed on cooling. The $Ni(TEP)Br_2$ was recrystallized from absolute alcohol and dried at 35°: m.p., 213°.

Dichlorodiphosphinenickel(II), $Ni(TEP)Cl_2$. A solution of 1·39 g (5·8 mmoles) of nickel(II) chloride six hydrate in 20 ml of absolute alcohol was added to 2·39 g (11·6 mmoles) of diphosphine in 15 ml of absolute ethanol. The resulting yellow-brown solution was evaporated until crystals formed, and was then cooled. Further evaporation gave a second crop of crystals. After recrystallization of the combined precipitates from absolute ethanol, 1·7 g of $Ni(TEP)Cl_2$ was obtained (89 per cent yield based on $NiCl_2{\cdot}6H_2O$). Part was again recrystallized and dried at 100°: m.p. (decomp.), 245–249°.

Bis(diphosphine)nickel(II) *perchlorate*. $[Ni(TEP)_2](ClO_4)_2$. Nickel(II) perchlorate six hydrate (0·42 g, 1·14 mmoles) was dissolved in 5 ml of absolute ethanol and added to 0·47 g (2·28 mmoles) of diphosphine. The yellow precipitate which formed immediately was recrystallized from methanol and dried at 55°.

Tribromodiphosphinenickel(III), $Ni(TEP)Br_3$. A benzene solution containing 0·0151 g (0·094 mmole) of bromme was added to a filtered solution of 0·08 g (0·189 mmole) of $Ni(TEP)_2Br_2$ in 80 ml of warm benzene. After cooling, the green-black precipitate was collected on a filter, and washed with benzene and ethyl ether.

Bis-(diphosphine)copper(I) *diiodiodiphosphinecuprate*(I), $[Cu(TEP)_2]\ [Cu(TEP)I_2]$. A mixture of 0·32 g (1·55 mmoles) of diphosphine and 0·46 g (2·41 mmoles) of copper(I) iodide in 5 ml of potassium iodide solution (saturated at room temperature) was shaken for 4 hr under nitrogen. The precipitate which formed was collected on a filter, washed with potassium iodide solution and water, recrystallized from benzene, and dried at 100°. $[Cu(TEP)_2]\ [Cu(TEP)I_2]$ is insoluble in water, ethanol and acetone: m.p., 181–183°.

Bis-(diphosphine)silver(I) *diiodoargentate*(I), $[Ag(TEP)_2]AgI_2$. This compound was prepared in the same manner as the copper(I) compound, using 0·52 g (2·21 mmoles) of freshly prepared silver iodide and 0·45 g (2·18 mmoles) of diphosphine in 10 ml of potassium iodide solution and shaking 17 hr. The colourless material was recrystallized from nitrobenzene, washed with benzene and ethyl ether, and dried.

Diiodo-μ-diphosphinedigold(I), IAu(TEP)AuI. A solution of 0·5 g (2·42 mmoles) of diphosphine in 10 ml of ethanol was added to 20 ml of ethanol saturated with sodium iodide (at room temperature). The solution was heated to boiling under a nitrogen blanket and 0·78 g (2·41 mmoles) of gold(I) iodide was slowly added with rapid stirring. White crystals formed in the boiling solution. The mixture was cooled and the precipitate of $Au_2(TEP)I_2$ was collected on a filter and recrystallized from acetone. The molecular weight, determined ebullioscopically in chloroform, is 820 (Calc. 854·5).

Hexaiodo-μ-diphosphinedigold(III), $I_3Au(TEP)AuI_3$. Two millilitres of chloroform containing 0·072 g (0·283 mmole) of iodine was added to 0·12 g (0·141 mmole) of $Au_2(TEP)I_2$ in 5 ml of chloroform. The black crystalline precipitate which formed was collected, washed with chloroform, and dried.

Dibromodiphosphinezinc, $Zn(TEP)Br_2$. A solution of 0·48 g (2·13 mmoles) of zinc bromide in 3 ml of absolute ethanol was added to 0·44 g (2·12 mmoles) of diphosphine in 2 ml of the same solvent. A white precipitate formed which changed into an oil. When cooled in an ice-bath, the oil solidified and the crude product was collected on a filter. To recrystallize the product, it was dissolved in hot dimethylformamide, the solution was filtered and while it was being heated, water was slowly added until the solution became cloudy. It was heated for an additional minute or two and cooled. The $Zn(TEP)Br_2$ was collected on a filter and dried. It is also soluble in chloroform.

Bromodiphosphine–cadmium complexes. A solution of 1·23 g (4·52 mmoles) of cadmium bromide in 10 ml of 50–50 alcohol–water mixture was added to 0·93 g (4·51 mmoles) of diphosphine. A white precipitate formed immediately, but the mixture was shaken for 3 hr to make sure the reaction was complete. The crude material was recrystallized by the method used for $Zn(TEP)Br_2$ and dried at 110°. The product was $Cd_3(TEP)_2Br_6$.

A sample of $Cd_3(TEP)_2Br_6$ was recrystallized from dimethylformamide by adding water, and was dried at 55°. This yielded the simple complex $Cd(TEP)Br_2$. $Cd(TEP)Br_2$ can be converted back to $Cd_3(TEP)_2Br_6$ by reaction with cadmium bromide (1 : 1 molar ratio) in dimethylformamide followed precipitation with water and recrystallization. The nature of the compound which precipitates must by depend on the relative amounts of $Cd(TEP)Br_2$ and $CdBr_2$ present.

Dichlorodiphosphinepalladium(II), $Pd(TEP)Cl_2$. A hot solution of 0·25 g (1·4 mmoles) of palladium-(II) chloride and 0·15 g (2·8 mmoles) of ammonium chloride in 10 ml of water was added to 0·29 g

(1·4 mmoles) of diphosphine and shaken for 3 hr under nitrogen. The pinkish-tan precipitate was collected on a filter and then dissolved in dimethylformamide. After a small amount of red-brown precipitate was filtered off, the solution was evaporated to a small volume. White crystals formed on standing. They were recrystallized from ethanol and dried at 50°.

The complex can also be prepared from $Pd(H_4EDTA)Cl_2$ and diphosphine: To 0·34 g (1·65 mmoles) of diphosphine in 5 ml of ethanol was added a solution of 0·95 g (1·66 mmoles) of $Pd(H_4EDTA)Cl_2 \cdot 5H_2O$[34] in 5 ml of the same solvent. Ethylenediaminetetraacetic acid precipitated. (Found: N, 9·34. Calc. N, 9·58%.) The filtrate was evaporated to a small volume and cooled. The $Pd(TEP)Cl_2$ was collected and recrystallized from absolute ethanol.

Several attempts were made to prepare *bis*(diphosphine) palladium(II) chloride. The reaction of tetraamminepalladium(II) chloride[35] with 2 moles of diphosphine using a charcoal catalyst gave dichlorodiphosphinepalladium(II). Attempts to make dichlorodiphosphinepalladium(II) react with diphosphine led only to recovery of the starting complex.

Dibromodiphosphinelead(II), $Pb(TEP)Br_2$. A filtered solution of 0·89 g (2·42 mmoles) of lead(II) bromide in 25 ml of hot potassium bromide solution (saturated at room temperature) was added to 0·33 g (1·6 mmoles) of diphosphine and the mixture was shaken for 5 hr under nitrogen. The white precipitate was filtered and washed with potassium bromide solution and then with water. The crude product was recrystallized twice from dimethylformamide and dried at 55°.

Bis-(diphosphine)lead(II) *perchlorate*, $[Pb(TEP)_2](ClO_4)_2$. When a solution of 2·09 g (4·55 mmoles) of lead(II) perchlorate three hydrate in 10 ml of ethanol was added to 1·87 g (9·08 mmoles) of diphosphine in 5 ml of ethanol, an oil separated. This solidified when cooled in an ice-bath. The cream coloured precipitate was recrystallized from a 50–50 alcohol–water mixture to yield 1·47 g (40 per cent) of $[Pb(TEP)_2](ClO_4)_2$. A small sample was recrystallized twice and dried: m.p. 150–152°.

Magnetic moments. Magnetic measurements were taken on a modified Curie–Cheneveau balance previously described.[36] Dimagnetic corrections were made according to SELWOOD.[37]

Conductivities. Conductivity measurements were made on a Leeds and Northup conductivity bridge (No. 4866). The nitrobenzene was fractionally crystallized three times, dried with phosphorus(V) oxide and distilled under reduced pressure. The middle fraction was used. The specific resistance of the water used was $3·12 \times 10^6$ ohms.

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X-RAY AND KINETIC STUDY OF THE HYDROGEN REDUCTION OF γ-UO_3*

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Abstract—The hydrogen reduction of γ-UO_3 to UO_2 was studied by X-ray examination of quenched samples and kinetic observations over the temperature range, 450–550°C, and hydrogen partial pressures between $\frac{1}{2}$ and 1 atm. The data were interpreted in terms of three consecutive reactions: $UO_3 \rightarrow U_3O_{8+}$, $U_3O_{8+} \rightarrow U_3O_{8-}$, $U_3O_{8-} \rightarrow UO_2$. In both the first and third steps, two solid phases are present; it is postulated that the second step involves the homogeneous transition between the upper and lower limits of the U_3O_8 structure. The rate of reaction is directly proportional to surface area. Rate data obtained for the first and third steps of the reaction are expressed as a function of temperature and hydrogen partial pressure: Rate (per unit surface) $= KP^n \exp(-E/RT)$. The pressure dependence exponent, n, is approximately 0·8. The activation energy, E, is 25·2 ± 2·0 kcal/mole for the reaction, $UO_3 \rightarrow U_3O_{8-}$, and 30·6 ± 1·8 kcal/mole for the reaction, $U_3O_{8-} \rightarrow UO_2$.

THE commercial processing of uranium ore concentrates involves the conversion of uranyl nitrate hexahydrate (UNH) to γ-UO_3 (orange oxide) by thermal decomposition, followed by reduction of this oxide to UO_2 with dissociated ammonia at elevated temperatures.[1] The reduction reaction is of interest from both a practical standpoint and as a study related to the uranium–oxygen system.

Although phase relationships in the uranium–oxygen system have not been fully defined, many of the oxides of multi-valenced uranium have been characterized, and their limits of homogeneous composition established with reasonable reliability. Only a brief summary of this system is given here; for more detailed descriptions, see KATZ and RABINOWITCH[2], GRONVOLD[3] and HOEKSTRA and SIEGEL[4] among others.

The oxides, UO_2, U_4O_9, U_3O_7, $U_5O_{13}(UO_{2\cdot6})$, U_3O_8 and UO_3, have been substantiated. The upper composition limit of cubic UO_2 increases with temperature; the composition range extends to $UO_{2\cdot1}$ at 500°C[3] and to $UO_{2\cdot3}$ at 1160°C[5]. Cubic U_4O_9 extends over only a narrow domain. Tetragonal U_3O_7 is unstable above 500°C, disproportionating into U_4O_9 and an orthorhombic phase.[6] The lower limit of orthorhombic U_3O_8 has been reported as $UO_{2\cdot56}$ at 500°C by GRONVOLD[3], while HOEKSTRA *et al.*[7] have found between the composition limits $UO_{2\cdot56}$ and

* This paper is based on the work performed for the Atomic Energy Commission by the National Lead Company of Ohio.

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$UO_{2\cdot65}$ another orthorhombic phase, $UO_{2\cdot6}$ (U_5O_{13}), which is very similar to U_3O_8. The latter authors also reported a metastable, β-orthorhombic form of U_3O_8 and above 400°C, a hexagonal form of U_3O_8. The "U_2O_5" phase reported by RUNDLE *et al.*[8] corresponds to U_5O_{13}, mentioned above. The region, U_3O_8–UO_3, has been observed as both heterogeneous and homogeneous, depending on the thermal history of the sample.[2]

Uranium trioxide exists in at least five crystalline modifications and an amorphous form. Using the nomenclature introduced by HOEKSTRA and SIEGEL[4], these crystalline forms are α (hexagonal), β (unknown structure), γ (probably orthorhombic), δ (cubic), and ε (unknown structure). The most stable form, γ-UO_3, has frequently been referred to as Type III, and is the form used in the study reported here.

In preliminary kinetic studies of the hydrogen reduction of UO_3, a variety of rate types were observed, many of them indeterminate but some of which approximated either linear, phase boundary limited or first order rates. This diversity of results suggested that the samples used differed in their physical properties, and that gross particle effects were obscuring the true kinetics. Since a linear rate (that is, a zero-order reaction) was the least encumbered of the various types observed, orange oxide samples which exhibited linear rates were used for the X-ray and kinetic study reported here.

MATERIALS AND METHODS

γ-UO_3 was prepared by the thermal decomposition of purified uranyl nitrate hexahydrate. Rate data were obtained with sample D-3; the X-ray study was conducted with sample C-2. Both samples, as originally prepared, contained nitrate and water (see Table 1). These impurities were driven off

TABLE 1.—COMPOSITION AND PROPERTIES OF UO_3 SAMPLES

	D-3	C-2
U content (%)	80·65	83·02
H_2O content (%)	2·62	0·10
NO_3 content (%)	0·47	0·26
U_3O_8 content (%)	0·20	0·09
Specific surface area* (m^2/g)	3·4	2·6
Mean particle size† (μ)	0·23	0·30
Real density* (g/cm^3)	7·73	7·62

* Determined after driving off water and nitrate by heating at 500°C for 30 min.

† Assuming that all particles exposed to gaseous contact are uniformly sized spheres or cubes, their mean diameter or edge length ($\bar{d}$) is calculated as:

$$\bar{d} = \frac{6}{\rho(SA)}$$

where ρ = real density SA = specific surface area.

immediately prior to making a kinetic run or preparing a partially reduced sample by heating for 15 min in the thermobalance at the temperature of the projected reduction, in an atmosphere of flowing helium. Both samples contained only trace amounts of cationic impurities.

Reaction rates were determined with an automatic recording thermobalance. The sample was suspended from a Gram-atic Model 1-910 balance and the weight was recorded continuously on a

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Schaevitz-modified Brown recorder which sensed the beam deflexion by means of a linear variable differential transformer mounted on the balance. Recorded weights were accurate to $\pm 0{\cdot}5$ mg and had a maximum range of 100 mg. The reaction tube was of quartz, 11 cm in diameter by 43 cm long, heated by a vertically-mounted tube furnace, and controlled isothermally by a West Model JS Stepless Controller. Reaction temperatures were determined with a calibrated thermocouple mounted just below the sample pan. The temperature during a run was constant within ± 1°C, and the estimated accuracy was ± 5°C.

For rate determinations, a 1·600 g sample of D-3 orange oxide screened to $-150, +200$ mesh size was placed in a 200-mesh platinum gauze basket 5·5 cm in diameter, forming a layer about 0·2 mm thick. After the loaded basket was suspended in the preheated reaction chamber, helium was allowed to flow for 15 min before admitting hydrogen. During this time temperature equilibrium was attained and the nitrate and water content of the UO_3 was driven off. The original sample weight was therefore corrected to give the true UO_3 weight, 1·552 g. The calculated weight loss for reduction to UO_2 is 87 mg. The observed losses were 86–87 mg. A total gas flow of 4 l/min was used; hydrogen partial pressures of less than one atmosphere were obtained by dilution with helium. Cylinder hydrogen was used directly; the helium was oxygen-gettered and dried by passage over hot UO_2, Drierite, and magnesium perchlorate.

The X-ray study was conducted with sample C-2 because the D-3 material was no longer available. The C-2 oxide was selected because its reduction curves were very similar to those of D-3. Partially reduced samples were prepared in the thermobalance by reducing to the desired compositions (as calculated after correcting for loss of water and nitrate) at about 400°C with H_2 at a low partial pressure. These mild reduction conditions were necessary in order to halt the reaction at the desired degree of conversion. Samples were quenched in a helium atmosphere by cooling the reaction tube with an air stream. Visual examination of the quenched samples showed uniform colouring throughout the entire bed, thus indicating homogeneous reaction. The composition of the products was determined accurately by calcining a weighed portion to U_3O_8 (30 min at 950°C in air). The product composition determined in this manner agreed with the calculated value within 0·02 moles of oxygen and the estimated accuracy was $\pm 0{\cdot}01$ moles of oxygen per mole uranium. X-ray diffraction patterns were obtained by means of a Norelco unit, using nickel filtered Cu radiation and a 114·6 mm camera.

KINETICS

Investigation of external physical factors that might be expected to affect the observed reduction rate gave the following results:

Sample size. For 0·5–4 g samples, the rate of reaction per gramme of sample and the time required to reach any given fraction of conversion were independent of the sample size. For larger samples, heat given off by the exothermic reaction temporarily upset isothermal conditions.

Bed depth. Variation of sample bed depth under 1 mm thickness had no effect on the reaction rate.

Gas flow rate. At 1 atm pressure, increasing the hydrogen flow from 1 to 4 l/min had no effect on the reaction rate.

Particle size. For a sample of 4 m^2/g surface area (equivalent to a mean particle size of 0·2 μ), identical reaction rates were obtained for gross particle size cuts of 0–5, 5–10, 10–60 and 0–105 μ.

From the above observations, it was concluded that the reduction rates per gramme of UO_3 observed for sample D-3 under the test conditions employed were independent of sample size, bed depth, gas flow rate and particle size.

Since surface area is a primary variable in a gas–solid reaction, this factor was investigated considering (1) variations in the surface area of the UO_3 starting material, and (2) the change in surface area as the reduction progressed. Surface areas were determined by the BET method, nitrogen being used as the adsorbate.

For orange oxide samples prepared in the laboratory under carefully controlled

conditions from a single UNH feed, where the specific surface area of the products was varied by altering the denitration conditions, the reduction rate per gramme was directly proportional to the specific surface area, as shown in Fig. 1.

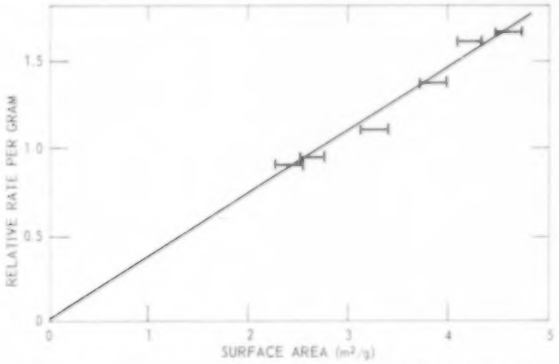

FIG 1.—Relationship between surface area and reduction rate of UO_3. Reduction rates determined with 1·60 g samples at a temperature of 500°C and a hydrogen pressure of 1 atm.

The specific surface area of a given sample was shown to remain essentially constant during reduction. For orange oxide C-2 with a surface area of 2·6m/g, a partially reduced sample of composition $UO_{2\cdot81}$ had an area of 2·1, and for composition $UO_{2\cdot28}$ the area was 2·2 m^2/g. For another orange oxide with ·75 m^2/g area, the partially reduced products had areas of 5·0 and 5·2 m^2/g at compositions $UO_{2\cdot81}$ and $UO_{2\cdot41}$, respectively. In both cases, the area decrease at composition $UO_{2\cdot81}$ was

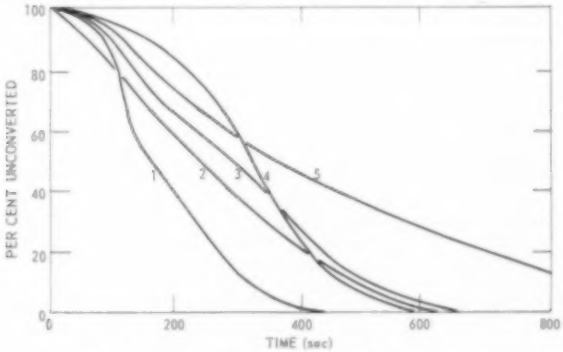

FIG. 2.—Some of the types of observed UO_3 reduction curves.
Curve 1—Pronounced two-step reaction.
Curve 2—No induction period; contains 2·5 per cent sulphate.
Curve 3—Pronounced three-step reaction.
Curve 4—Extreme induction period; contains 0·5 per cent sulphate.
Curve 5—Phase-boundary type.
Reduction conditions: Temperature, 500°C; Hydrogen pressure, 1 atm.

about five times greater than the change calculated on a molar volume basis, indicating that some sintering had occurred. The small increase in area of the low oxygen compositions suggested that a limited amount of particle breakdown had occurred.

The reduction curves of orange oxides exhibit a variety of shapes; Fig. 2 depicts

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some of the varieties obtained. Both the manner of denitration of UNH and the use of additives in ppm amounts affect the shape of the curve and the over-all rate of reaction. Generally, those samples that reduced the fastest exhibited linear rates

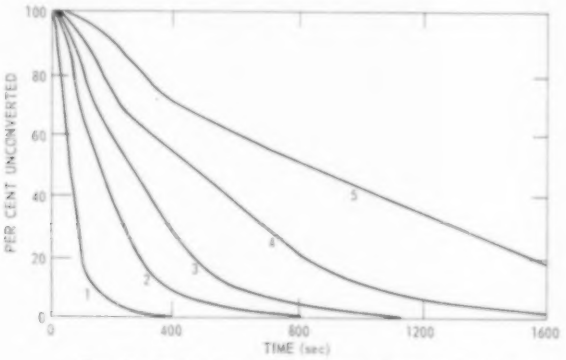

FIG. 3.—Typical reduction curves of orange oxide D-3.
Curve 1—1 atm H_2, 552°C
Curve 2—1 atm H_2, 504°C
Curve 3—$\frac{1}{2}$ atm H_2, 504°C
Curve 4—$\frac{1}{4}$ atm H_2, 504°C
Curve 5—$\frac{1}{2}$ atm H_2, 452°C.

and one or two relatively sudden rate changes. Samples of this type were considered to be more nearly representative of the true reaction kinetics, and the deviations of other types ascribed to particular physical characteristics of those types, such as degree and nature of agglomeration and distribution of particle and crystallite sizes.

Typical reduction curves for D-3 orange oxide are shown in Fig. 3. These curves may be generally described as follows, in terms of increasing degree of conversion:

UO_3–$UO_{2.9}$: increasing rate
$UO_{2.9}$–$UO_{2.7}$: constant rate
$UO_{2.7}$–$UO_{2.6}$: decreasing rate, with a linear region for the more slowly reacting samples
$UO_{2.6}$–$UO_{2.1-2.2}$: constant rate
$UO_{2.1-2.2}$–UO_2: decreasing rate

Kinetically, the reduction was considered to consist of three stepwise reactions:

(1) the conversion of UO_3 to $\sim U_{2.7}$
(2) the conversion of $\sim UO_{2.7}$ to $\sim UO_{2.6}$
(3) the conversion of $\sim UO_{2.6}$ to UO_2.

The accelerating portion of the first step reflects the approach to a steady state. The tailing during the last part of the third step may be caused by either nonuniform crystallite size or poor gas accessibility to the centers of some gross particles—it does not seem to be a systematic function of the degree of conversion.

The linear regions of the first and third steps, as specified above, were used to determine reaction rates for those steps, in milligrams of weight loss per sec per square metre of surface area, and are tabulated in Table 2. Rates are not given for the second step, $UO_{2.7} \rightarrow UO_{2.6}$, since the short duration of this reaction, particularly at the higher temperatures, did not permit the accurate determination of rates.

The temperature dependence of the first and third reaction steps was determined by least-squares treatment of Arrhenius plots. The activation energies were 25·2 ± 2·0 kcal and 30·6 ± 1·8 kcal for the first and third steps, respectively, at a hydrogen pressure of one atmosphere. The activation energy values obtained at the lower hydrogen pressures were within these 95 per cent confidence intervals.

TABLE 2.—REDUCTION RATES OF UO_3; SAMPLE D-3

	Rate (mg/sec per m² of UO_3 surface)	
	First step $UO_3 \rightarrow U_3O_{8+}$	Third step: $U_3O_{8-} \rightarrow UO_2$
552°C		
1 atm	0·256	0·141
½ atm	0·160	0·075
¼ atm	0·079	0·041
530°C		
1 atm	0·172	0·0761
504°C		
1 atm	0·103	0·0438
½ atm	0·057	0·0252
¼ atm	0·033	0·0129
479°C		
1 atm	0·0643	0·0221
452°C		
1 atm	0·0302	0·01056
½ atm	0·0175	0·00622
¼ atm	0·0107	0·00381

The pressure dependence of both reaction rates was expressed as an exponential function of the hydrogen partial pressure, Rate $\propto P^n$. The value of n was determined by means of log–log plots, and was found to be 0·83 for the first step and 0·89 for the third step at 550°C, both values decreasing slightly at 500°, and then decreasing to 0·75 at 450°C.

X-RAY STUDIES

Diffraction data were obtained for fourteen samples prepared from C-2 oxide, covering the composition range UO_3 to UO_2. The X-ray data, which are summarized in Table 3, suggest that γ-UO_3 is reduced stepwise, first to a U_3O_{8+} phase, then to a U_3O_{8-} composition, and finally to UO_2.

The only phases detected at room temperature were γ-UO_3, orthorhombic U_3O_8 and a cubic phase. Hexagonal U_3O_8, β-U_3O_8, U_5O_{13} and U_3O_7 were not observed. The X-ray data indicate that the cubic phase was UO_2, and not U_4O_9 or UO_{2+}, throughout its entire range of observation. Arguments against the formation of

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U_4O_9 as a stable intermediate are also provided by the observation of the U_3O_8 phase at compositions $UO_{2.23}$ and $UO_{2.13}$ and by the absence of a rate change at composition $UO_{2.25}$ during reduction. However, the possibility of a UO_{2+} phase cannot be ruled out.

TABLE 3.—X-RAY DIFFRACTION DATA

Composition*	Phases		
	γ-UO_3	U_3O_8	Cubic
$UO_{3.03}$†	×		
$UO_{2.99}$	×	×(Very weak)	
$UO_{2.93}$	×	×	
$UO_{2.84}$	×	×	
$UO_{2.77}$	×	×	
$UO_{2.74}$	×(Very weak)	×	
$UO_{2.70}$		×	
$UO_{2.63}$		×	
$UO_{2.59}$		×	×(Weak)
$UO_{2.56}$		×	×
$UO_{2.33}$		×	×
$UO_{2.23}$		×	×
$UO_{2.13}$		×(Very weak)	×
$UO_{2.02}$			×

× indicates that the phase is present.
* As determined by calcination to U_3O_8.
† Starting material sample C-2. The apparent oxygen content of this sample also includes nitrate and water.

Since X-ray diffraction is not very sensitive for minor components, the limits of detection of UO_2, U_3O_8 and γ-UO_3 in admixtures with uranium oxides were determined to provide a basis for correcting the observed compositions where a minor phase was first ot last detected. These lower limits were: 8% γ-UO_3 in U_3O_8, 2% UO_2 in U_3O_8 and 9% U_3O_8 in UO_2, for samples crystallized at about 500°. Application of these factors to the data in Table 3 corrects the limits of composition of two-phase mixtures as follows: lower limit of γ-UO_3 and U_3O_8, $UO_{2.72}$; upper limit of U_3O_8 and UO_2, $UO_{2.59}$; lower limit for U_3O_8 and UO_2, $UO_{2.09}$.

The early appearance of U_3O_8 at a composition corresponding to only 3% U_3O_8 suggests that kernels of U_3O_8 are initially formed on the surface of the UO_3. It also indicates that, under reduction conditions, there is no appreciable region of solid solution of U_3O_8 in γ-UO_3

DISCUSSION

On the basis of the X-ray and kinetic data, it is postulated that the hydrogen reduction of γ-UO_3 proceeds in three consecutive reactions:

$$UO_3 \rightarrow U_3O_{8+} \quad (1)$$

$$U_3O_{8+} \rightarrow U_3O_{8-} \quad (2)$$

$$U_3O_{8-} \rightarrow UO_2 \quad (3)$$

The first reaction is the diphasic transformation of γ-UO_3 to orthorhombic U_3O_{8+}, the upper composition limit of U_3O_8. The second reaction is the homogeneous transition from the upper to the lower composition limits of the U_3O_8 structure. The third reaction is the conversion of U_3O_{8-} to a cubic structure. The above reaction sequence requires that either equilibrium or a steady state be attained in the solid phase. This is possible if the rate of reaction is restricted at the surface of the solid, permitting oxygen to diffuse through the solid to the surface as fast as it is abstracted.

Rate data, supported by the diffraction data, provide direct evidence that the reduction reaction is limited by the rate of surface reaction. In the simple case where solid *A* reacts with a gas to yield solid *B*, the conversion versus time curve is linear only* if the reaction rate is limited by a surface process such as adsorption, chemisorption or chemical reaction at active sites. Other rate-limiting mechanisms (diffusion, nucleation and growth, solid-solid phase interface reaction) yield parabolic, cubic, logarithmic, sigmoidal or other non-linear rate expressions. The various rate laws have been discussed by other authors.[6,9,10] In the more complex case, where solid *A* reacts with a gas to yield first solid *B*, then solid *C* and finally solid *D*, each reaction may be considered independently if each goes to completion in sequence, which the diffraction data indicate occurs in this case. The first reaction, $UO_3 \rightarrow U_3O_{8+}$, is linear after an initial period of accelerating rate. This induction period probably indicates the time required to form a complete layer of U_3O_{8+} around each UO_3 crystallite, although it might also be caused by the time required for hydrogen to displace helium from all the micropores.

The rate of the second reaction, $U_3O_{8+} \rightarrow U_3O_{8-}$, could not be quantitatively defined because of its short duration. However, during some of the slower reductions, this step did exhibit a linear portion.

The third reaction, $U_3O_{8-} \rightarrow UO_2$, is linear except for the final part of the conversion. This tailing might be caused by external physical factors, as mentioned before, or by the formation of a continuous series of non-stoicheiometric cubic oxides in the range $UO_{2\cdot1}$–UO_2.

Phase data are in agreement with the postulated three-step reaction sequence. The non-solubility of U_3O_8 in UO_3, at least under some conditions, has been reported.[2] BILTZ and MÜLLER[5] obtained compositions of the type U_3O_{8+} by decomposing UO_3 at various oxygen pressures. The U_3O_{8-} structure has been established.[3,5,7,11] The upper limit of the cubic UO_2 structure is about $UO_{2\cdot1}$ at the temperatures at which reduction was carried out.[3]

Other reduction studies of uranium oxides also indicate that reduction occurs in a sequence of reactions. GRONVOLD[3] found that the reduction of U_3O_8 with hydrogen at 330°C yielded orthorhombic $UO_{2\cdot56}$. ARONSON and CLAYTON[12] concluded that U_4O_9 was first reduced to UO_{2+x} ($0{\cdot}06 > x > 0{\cdot}10$) and then to UO_2, at temperatures of 400–600°C. DEMARCO and MENDEL[13] observed that "high surface area" UO_3

* Exceptions can be devised, but they depend upon very special properties: the solid must be in the form of thin platelets, or the reaction must proceed preferentially in one direction through a uniform cross-section. Neither of these exceptions applies in this case.

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[13] R. E. DEMARCO and M. G. MENDEL, *J. Phys. Chem.* **64**, 132 (1960).

reduced first to $UO_{2\cdot56}$ and then to UO_2. The oxidation of UO_2 was also found to occur as a two-reaction sequence: $UO_2 \rightarrow U_3O_7$ and $U_3O_7 \rightarrow U_3O_8$.[9]

The rate of hydrogen reduction of γ-UO_3 should therefore be considered in terms of the three sequential reactions that have been postulated. The rate of each individual reaction may be expressed by the general equation,

$$\text{Rate (in mg/sec per m}^2) = K P^n \exp(-E/RT)$$

where K = proportionality constant, P = partial pressure of hydrogen, n = pressure dependence exponent, E = activation energy.

The values of the above constants for the reactions, $UO_3 \rightarrow U_3O_{8+}$ and $U_3O_{8-} \rightarrow UO_2$, are tabulated below:

Reaction	$UO_3 \rightarrow U_3O_{8+}$	$U_3O_{8-} \rightarrow UO_2$
K	$1{\cdot}12 \times 10^6$	$15{\cdot}8 \times 10^6$
n	0·8	0·8
E	25·2	30·6

The values of n and E reported by ARONSON and CLAYTON[12] and DEMARCO and MENDEL[13] and the values for K (mg/sec per m²) calculated from their data are listed below, for comparison with the above constants: ARONSON and CLAYTON ($U_4O_9 \rightarrow UO_2$)

Sample	*B*	*C*
Surface Area (m²/g)	1·75	0·45
K	$0{\cdot}266 \times 10^6$	$0{\cdot}162 \times 10^6$
n	0·7	0·7
E	25	25

DEMARCO and MENDEL (surface area, 26 m²/g)

Reaction	$UO_3 \rightarrow UO_{2\cdot56}$	$UO_{2\cdot56} \rightarrow UO_2$
K	$1{\cdot}81 \times 10^6$	3620×10^6
n	0·6	0·4
E	27·2	39·6

In a heterogeneous reaction, the surface characteristics of the solid may greatly affect the rate of reaction. Since surface characteristics are notoriously variable, the preceding constants show relatively good agreement for corresponding reactions, with three exceptions. These are: (1) the high activation energy for $UO_{2\cdot56} \rightarrow UO_2$,

(2) the very large (20,000-fold) variation in K for the reaction leading to UO_2 and (3) the low values of n obtained by DEMARCO and MENDEL.

No explanation is apparent for the large activation energy. It may have resulted from impurities.[14]

The large variation in the proportionality constant, K, which includes the factor, number of active sites per unit area, can be explained qualitatively. The U_4O_9 samples of ARONSON and CLAYTON were prepared by a sintering and annealing technique which would tend to decrease the number of active sites per unit area, thus decreasing K. DEMARCO and MENDEL started with an active, possibly metastable form of UO_3, which on reduction to $UO_{2.56}$ at low temperatures could easily yield a highly disoriented product with a high concentration of active sites. In the present work, the most stable form of UO_3 was used as a starting material, but the intermediate oxide was formed *in situ* and not annealed. Thus, an intermediate value would be expected for K, as was observed. Another factor is the structure of the source material. U_4O_9 was prepared from cubic UO_2. The other oxides were derived from orthorhombic structures.

The lower values of n were obtained by DEMARCO and MENDEL at 300–400°C, as compared to 400–600°C by ARONSON and CLAYTON. In the present work, a corresponding variation of n with temperature was noted, the value decreasing from about 0·85 at 550°C to about 0·75 at 450°C. The fractional value of n, and its variation with temperature, are also evidence that the reduction reaction is limited by the rate of surface reaction. LANGMUIR's treatment shows that as the fraction of available sites occupied increases from zero to unity, n decreases from one to zero.[15] At lower temperatures, where the reaction rate is slower, a greater fraction of the available sites should be occupied, thereby causing n to decrease, as observed.

Based on ROBERTS' work,[16] it is probable that rate of chemisorption of hydrogen on the solid surface is the actual rate limiting step among the various surface processes. For a UO_2 surface, he finds that chemisorption occurs at measurable rates above 400°C and that the activation energy is about 35 kcal. He concludes that his "results are compatible with hydrogen adsorption taking place on oxygen sites."

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THE SOLUBILITIES OF LANTHANUM CHLORIDE 7-HYDRATE AND LANTHANUM CHLORIDE 6-HYDRATE IN WATER, AND A STUDY OF THE THERMAL DECOMPOSITION OF HYDRATED LANTHANUM CHLORIDE*

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Abstract—Thermal decomposition of $LaCl_3 7H_2O$ results in the stepwise formation of $LaCl_3 3H_2O$, $LaCl_3 \cdot H_2O$, $LaCl_3$ and LaOCl. Under proper conditions either $LaCl_3 6H_2O$ or $LaCl_3 7H_2O$ may separate from aqueous solutions of lanthanum chloride. The solubilities of the 6- and 7-hydrates at various temperatures are given.

THE solubility of $LaCl_3 7H_2O$ was measured in the 0–92° range by FRIEND and HALE[1]. If their data are plotted in terms of grammes of anhydrous $LaCl_3$ per 100 grammes of solution the results are fairly consistent, but when the data are plotted as grammes of $LaCl_3 7H_2O$ per 100g of water there is considerable deviation from a smooth curve. Although $LaCl_3 6H_2O$ has been described as triclinic by MARIGNAC[2] who reported the axial ratios to be 1·1593 : 1 : 0·8659 and the angles to be $\alpha = 91°3'$; $\beta = 114° 28'$; and $\gamma = 88° 12'$, there has been some doubt about the actual existence of $LaCl_3 6H_2O$. SODERSTROM,[3] for example, obtained crystals of $PrCl_3 7H_2O$ which had the same form as MARIGNAC's $LaCl_3 6H_2O$. It is known, furthermore, that $LaCl_3 \cdot 7H_2O$ is the hydrate generally encountered. IVERONOVA *et al.*[4] more recently have reported the structure of triclinic $LaCl_3 nH_2O$ which they assigned to the space group C_i^1–$P\bar{1}$. The lattice constants reported are:

$a = 8{\cdot}0$ kX	$\alpha = 72°$	$Z = 2$
$b = 8{\cdot}1$ kX	$\beta = 72° 30'$	
$c = 9{\cdot}1$ kX	$\gamma = 81°$	

Since they did not assign a definite hydrate number to their material, their work does little toward clarifying the situation regarding the hydrates of lanthanum chloride.

WENDLANDT[5] studied the thermal decomposition of $LaCl_3 7H_2O$ on a thermobalance, but due to his rapid rate of heating (5·4°C per min) he only found levels which corresponded to $LaCl_3 7H_2O$, $LaCl_3$ and LaOCl. In the case of praseodymium chloride, however, he picked up the level corresponding to $PrCl_3 H_2O$ as well as levels

* Contribution No. 792. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

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for $PrCl_3 7H_2O$, $PrCl_3$ and PrOCl. He failed to resolve the $PrCl_3 3H_2O$ level reported earlier by MATIGNON[6] who prepared $PrCl_3 7H_2O$, $PrCl_3 6H_2O$, $PrCl_3 3H_2O$, $PrCl_3 H_2O$ and $PrCl_3$. Because of the fact that $PrCl_3 3H_2O$ was known, but not $LaCl_3 3H_2O$, it was decided to study the thermal decomposition of $LaCl_3 7H_2O$ using a slower rate of decomposition than WENDLANDT used in his investigations. It was also decided to redetermine the solubility of $LaCl_3 7H_2O$ and to investigate the solubility of any other hydrates of lanthanum chloride which were stable in the presence of water.

Preparation of the $LaCl_3 7H_2O$

Five kilograms of La_2O_3, obtained in better than 99·9 per cent purity by the ion-exchange method of POWELL and SPEDDING[7], were dissolved in a slight excess of hydrochloric acid. The material was then recrystallized repeatedly from water to eliminate any excess acid. A sample of moist $LaCl_3 7H_2O$ that had been recrystallized six times was used in the following experiments.

The thermal decomposition of $LaCl_3 7H_2O$

An old Christian Becker analytical balance was converted to a thermobalance by altering the left-hand pan support so that a small quartz rod fastened above the beam of the balance would project through a hole drilled in the top of the case. A small stainless steel platform was installed on the end of the quartz rod and encased in a vertically-mounted furnace, so that a small platinum-foil tray of hydrate could be warmed and weighed simultaneously. In order to avoid changes in the moisture content of the air surrounding the sample, the furnace was continually flushed with air that was first bubbled through a bottle of H_2SO_4 solution (specific gravity = 1·337). This maintained the partial pressure of water in the furnace equal to about 10 mm of mercury. The temperature of the furnace was regulated by means of a variable transformer and a Brown Electronik controller-recorder activated by an iron–constantan thermocouple. The essential features of the thermal balance are shown in Fig. 1.

Samples of $LaCl_3 7H_2O$, recrystallized from water six times and weighing 0·5–1·0 g, were placed in the thermobalance and slowly heated until a weight loss was observed. The temperature was then held constant by means of the controller until no further loss occurred. When evolution of water ceased, the temperature was again increased gradually until the next break appeared. Pronounced levels corresponding to $LaCl_3 7H_2O$, $LaCl_3 3H_2O$, $LaCl_3 H_2O$ and $LaCl_3$ were observed, although the temperatures at which the weight breaks appeared depended somewhat on the rate of rise of the temperature. In the best controlled experiment $LaCl_3 7H_2O$ was converted to $LaCl_3 3H_2O$ between 53 and 54°, $LaCl_3 3H_2O$ was converted to $LaCl_3 H_2O$ at 90–96° and the monohydrate decomposed between 130 and 135°C. In all cases the loss of weight corresponding to the formation of anhydrous $LaCl_3$ was a few milligrams high, indicating a small amount of hydrolysis to LaOCl, but the main decomposition to LaOCl did not occur until between 360 and 550°C. In WENDLANDT's experiment no further weight loss occurred from 680 to 850°, indicating that LaOCl is quite stable. For details of the decomposition see Fig. 2.

[6] C. A. MATIGNON, *Ann. Chim. Phys.* (8) **8**, 364 (1906).
[7] J. E. POWELL and F. H. SPEDDING, *Chem. Engng. Progr.* (*Symposium Series*) **55**, No. 24, 101 (1959); U.S.A.E.C. Reports ISC 617 (1955) and ISC 875 (1958).

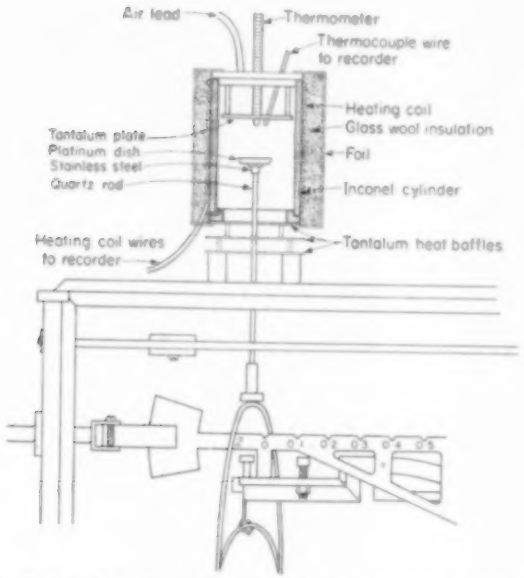

FIG. 1.—Design of the thermobalance used to study the decomposition of hydrated lanthanum chloride.

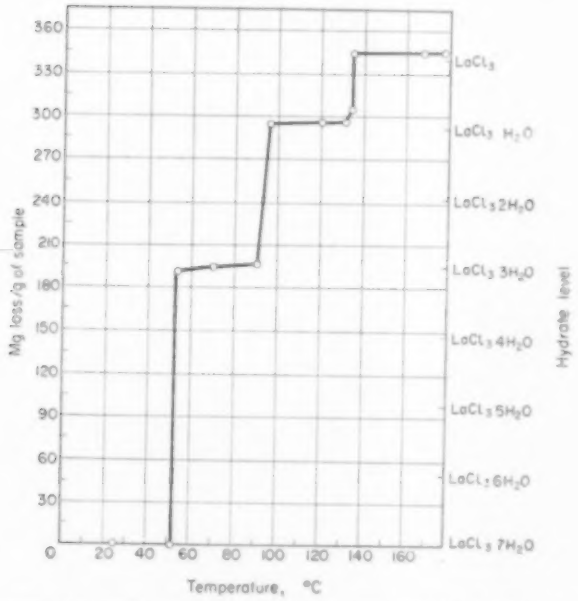

FIG. 2.—The thermal decomposition of hydrated lanthanum chloride in air in which the partial pressure of water is equivalent to 10 mm Hg.

The solubility of $LaCl_3 7H_2O$

Varying amounts of water were added to samples of $LaCl_3 7H_2O$ contained in one-ounce serum bottles. The samples were heated until all the $LaCl_3 7H_2O$ dissolved and then cooled to the desired temperature in a thermostatically controlled oil bath (neoprene stoppers were used because of the oil). A small crystal of $LaCl_3 7H_2O$ was then added to each supersaturated solution and the phases were allowed to equilibrate 24–48 hr. After equilibrium was attained, samples of the aqueous phase weighing about 0·5 g were withdrawn and weighed directly into crucibles which had been ignited to constant weight at 800°C. A millilitre of concentrated nitric acid was next added to each sample in order to convert the chloride to the nitrate. After standing

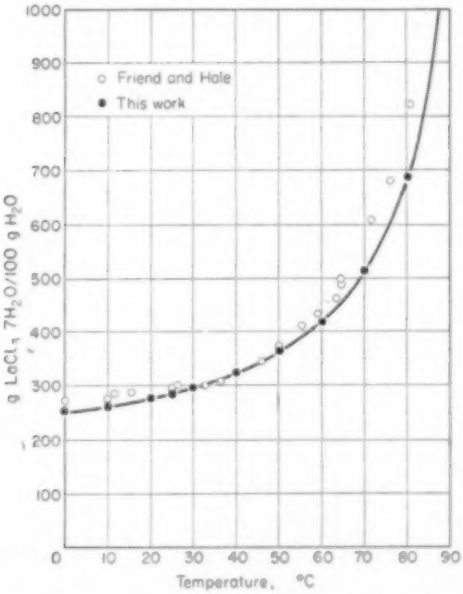

FIG. 3.—The solubility of lanthanum chloride 7-hydrate in water as a function of temperature.

about an hour at room temperature, the solutions were heated gently under an infra-red heat lamp until the evolution of brown fumes ceased. Then the samples were heated more strongly under heat lamps until a solid residue resulted. Next, the samples were heated carefully one at a time in the flame of a bunsen burner until the residue melted, decomposed with the evolution of brown fumes, and again solidified. Finally, the crucibles were reheated to 800°C in a muffle furnace, cooled over anhydrous magnesium perchlorate in a desiccator and reweighed. From the weight of oxide recovered and the original weight, the solubility of $LaCl_3 7H_2O$ per 100 g of water was calculated. The data are tabulated in Table 1 and plotted in Fig. 3 along with the data of FRIEND and HALE (*loc. cit.*). Comparing two sets of data, it appears that either FRIEND and HALE's supersaturated solutions had not yet attained equilibrium with the $LaCl_3 7H_2O$ phase or they allowed their oxide residues to absorb moisture during their weighing operations. In air La_2O_3 rapidly absorbs moisture and CO_2.

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The solubility of $LaCl_3 6H_2O$

During experiments at elevated temperatures, a solid phase was observed that was definitely not the usual $LaCl_3 7H_2O$. When crystals of $LaCl_3 7H_2O$ were heated above

TABLE 1.—THE SOLUBILITY OF $LaCl_3 7H_2O$ IN WATER*

Temperature (°C)	$LaCl_3 7H_2O/H_2O$ (g/100 g)	Temperature (°C)	$LaCl_3 7H_2O/H_2O$ (g/100 g)
0	251·6	60	415
10	258·9	70	512
20	275·5	80	686
25	284·5	90	1500
30	294·9	94	6300
40	321·7	95	∞
50	364·3		

95°C they melted to form a clear liquid. When this liquid was allowed to cool to about 60°C and then shaken, a solid phase separated with the evolution of appreciable heat. When the mixture of fine crystals and the solution in equilibrium with them was cooled to about 37°, a transformation to the usual $LaCl_3 7H_2O$ took place with the evolution of more heat. It was found that the phase which separated at 60° would redissolve if the mixture were heated above 70°, but that the product which formed at 37° would not remelt until a temperature of 95° was reached. By carefully reheating the mixture resulting at 60° to about 70° so that most of the solid dissolved and then cooling slowly, crystals of fair size were obtained. After draining off as much of the syrupy saturated solution as possible, some of the crystals were dislodged and blotted between pieces of filter paper. This procedure was not entirely successful because the disturbance caused the less soluble $LaCl_3 7H_2O$ to separate from the aqueous phase still clinging to the crystals of $LaCl_3 6H_2O$, giving them a frosted appearance. Nevertheless, analyses showed that these crystals contained between six and six and a half moles of water per mole of lanthanum chloride. It was concluded, therefore, that they

TABLE 2.—THE SOLUBILITY OF $LaCl_3 6H_2O$ IN WATER

Temperature (°C)	$LaCl_3 6H_2O/H_2O$ (g/100 g)	Temperature (°C)	g $LaCl_3 6H_2O$/100 g H_2O (g/100 g)
40	526	60	850
45	576	65	1200
50	621	70	2100
55	750	71·2	2300
		72·5	2700

were the elusive $LaCl_3 6H_2O$. It was subsequently possible to equilibrate mixtures of this new phase with its attendant solution at temperatures from 40° to 70°C and thus obtain solubility data. By pouring most of the water-rich phase off the crystals of

$LaCl_3 6H_2O$, remelting the residue and allowing the phase to reform, it was possible to approach the composition $LaCl_3 6H_2O$ more closely and obtain solubility data at temperatures up to the neighbourhood of 72°C. Solubility data for $LaCl_3 6H_2O$ are given in Table 2 and the solubilities of $LaCl_3 \cdot 7H_2O$ and $LaCl_3 \cdot 6H_2O$ are compared in Fig. 4.

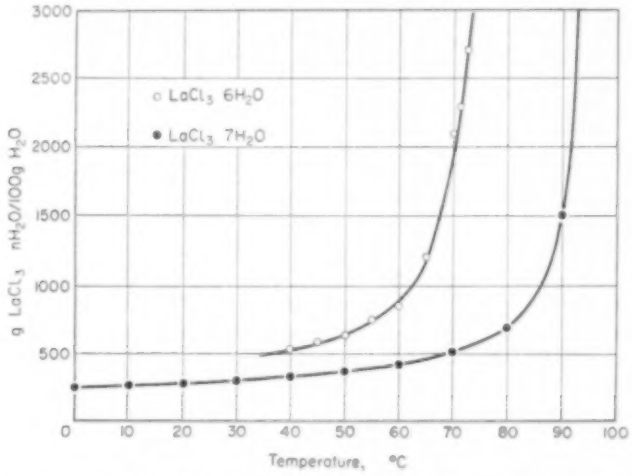

FIG. 4.—The solubility of lanthanum chloride 6-hydrate compared to the solubility of lanthanum chloride 7-hydrate.

DISCUSSION

It is apparent from the present work that lanthanum chloride forms 1-, 3-, 6- and 7-hydrates. Both $LaCl_3 7H_2O$ and $LaCl_3 6H_2O$ separate readily from aqueous solution under proper conditions, but $LaCl_3 7H_2O$ is the more stable of the two in the presence of water. The 6-hydrate is considerably more soluble in water than the 7-hydrate. $LaCl_3 3H_2O$, $LaCl_3 H_2O$ and $LaCl_3$ can be prepared by dehydrating $LaCl_3 7H_2O$, but some hydrolysis occurs unless the dehydration is carried out in an atmosphere of HCl. When $LaCl_3 7H_2O$ is heated to 800° in air, LaOCl is the end product. When heated at 53–54°C, $LaCl_3 7H_2O$ decomposes directly to $LaCl_3 3H_2O$. Evidence of the intermediate hydrate, $LaCl_3 6H_2O$, is not observed in thermolysis experiments.

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ÜBER NIOBSÄUREN UND WASSERLÖSLICHE ALKALINIOBATE—I

LICHTABSORPTIONS- UND DIFFUSIONSMESSUNGEN AN ALKALINIOBATLÖSUNGEN

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(*Received* 19 *September* 1959)

Abstract—U.V.-spectrophotometric studies with aqueous solutions of potassium and sodium niobates within the pH-region 5–14 results in an appearance of three different spectra; thus the existence of three individual types of polyniobate is probable. From diffusion measurements it is shown, that in strong alkaline solutions of potassium niobate (pH 11–14) anionic weights of nearly 1000 predominate, whereas in less alkaline solutions (pH < 9) a high polymer species with roughly a threefold weight exists.

IM Zusammenhang mit den seit Dezennien durchgeführten systematischen Untersuchungen hydrolysierender Systeme haben wir uns nun auch mit der Chemie der Niobsäuren und ihrer Alkalisalze befasst. Obwohl einige Informationen über dieses Gebiet in der älteren und neueren chemischen Literatur zu finden sind, kann man daraus keinen umfassenden Überblick über die in wässrigen Niobatlösungen vorliegenden Hydrolysegleichgewichte gewinnen. Das Ziel unserer Untersuchungen ist daher die Aufstellung eines Hydrolyseschemas, aus dem Zusammensetzungen und Aggregationsgrade der existierenden Niobsäuren bzw. deren Salze, ihre Beständigkeitsbereiche und gegenseitigen Beziehungen übersichtlich hervorgehen.*

Lichtabsorptionsmessungen

Zur Untersuchung hydrolysierender Systeme haben sich Lichtabsorptionsmessungen ausgezeichnet bewährt. Finden nämlich in den Lösungen schwacher anorganischer Sauerstoffsäuren bzw. derer Salze bei Änderung des pH-Wertes Kondensationsvorgänge unter Ausbildung von Sauerstoffbrücken statt, dann gehen ganz charakteristische Veränderungen der Lichtabsorptionsspektren parallel.

In der chemischen Literatur finden sich bisher keine Angaben über das optische Verhalten von Niobatlösungen. Um deshalb zunächst einmal Hinweise zu erhalten, in welchen pH-Bereichen mit der Existenz verschieden aggregierter Teilchen zu rechnen ist, haben wir optische Messungen von Kalium- und Natriumniobatlösungen mit pH-Werten von 5–14 durchgeführt. Rein wässrige Alkaliniobatlösungen reagieren infolge partieller Hydrolyse alkalisch. Zur Erzielung hoher pH-Werte wurden die Kaliumniobatlösungen mit KOH versetzt. Eine Abstumpfung der von Hause aus vorhandenen Hydroxylionenkonzentration erreichten wir durch Einleiten von CO_2 in die Niobatlösungen. Unabhängig von welchem Alkalisalz ausgegangen wurde, erhielten wir bei gleichen pH-Werten stets identische Absorptionsspektren. Der

* Wegen des vorliegenden umfangreichen Versuchsmaterials haben wir uns entschlossen, eine in drei Teile gegliederte Mitteilungsserie zu publizieren.

Lichtabsorptionsbereich der Alkaliniobatlösungen liegt zwischen ca. 210 und 300 mμ. Die Absorptionskurven steigen sämtlich steil an und erreichen im Gebiet 230–250 mμ mehr oder weniger gut ausgeprägte Maxima mit log ε-Werten zwischen 3 und 4. Längeres Kochen der Lösungen unter Rückfluss und CO_2-Ausschluss oder Aufnahme der Absorptionsspektren nach längerem Stehen der Lösungen blieb ohne Einfluss auf die Messergebnisse. Daher darf angenommen werden, dass Gleichgewichte, deren Einstellung merklich zeit- oder temperaturabhängig ist, nicht vorliegen.

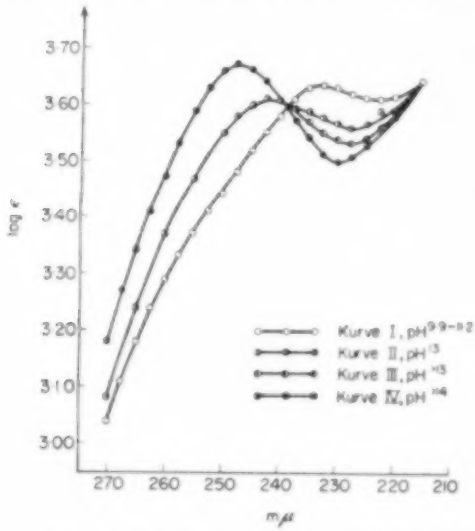

ABB. 1.—Absorptionsspektrum im pH-Gebiet 10–14.

Wir studierten zunächst die Änderungen, die sich bei allmählicher Erhöhung des pH-Wertes wässriger Kaliumniobatlösungen im Absorptionsspektrum abzeichneten. Aus den in Abbildung 1 dargestellten Absorptionskurven geht hervor, dass im pH-Gebiet 13–14 ein Gleichgewicht zwischen zwei Niobatanionen existieren muss. Sämtliche Kurven haben bei etwa 240 mμ einen gemeinsamen Schnittpunkt einen isosbestischen Punkt, der charakteristisch für das Vorliegen eines binären Gleichgewichtes ist. Die Reversibilität dieses Gleichgewichtszustandes ergibt sich aus der Feststellung, dass bei einer Verminderung der Hydroxylionenkonzentration der stark alkalischen Lösungen z.B. durch Einleiten von CO_2-das Absorptionsspektrum innerhalb der durch die Kurven I und IV sowie durch den isosbestischen Punkt gegebenen Grenzen gewissermassen rückläufig wird. Kaliumniobatlösungen mit $>$3 Mol KOH pro Liter scheiden allmählich kristallines Kaliumniobat aus und sind für unsere absorptiometrischen Untersuchungen nicht brauchbar, da sie sich offensichtlich nicht in einem stabilen Gleichgewichtszustand befinden. Diese Tatsache setzte unserem Bestreben nach Untersuchung extrem alkalischer Niobatlösungen eine obere Grenze.

Alkaliniobatlösungen mit pH-Werten $<$9 besitzen ein völlig anderes Absorptionsspektrum. In eine 0·2 prozentige Natriumniobatlösung wurde ein mässig schneller CO_2-Strom eingeleitet, nach 0, 2, 5, 10, 20 und 40 Minuten je eine aliquote Probe entnommen, auf das zehnfache Volumen verdünnt, ultrafiltriert und jeweils die

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Lichtabsorption gemessen. Die resultierenden Kurven sind in Abb. 2 dargestellt; die Absorptionsspektren der nach 10 (pH 5·4), 20 (pH 5·0) und 40 Minuten (pH 4·7) entnommenen Proben sind mit Kurve III (pH 6·5) identisch. Aus diesen Versuchsergebnissen geht hervor, dass sich das zunächst vorliegende Niobatanion (Kurve I; identisch mit Kurve I der Abb. 1) unter dem Einfluss zunehmender Wasserstoffionenkonzentration in ein Niobatanion anderer Konstitution umwandelt, welches innerhalb des pH-Bereichs <9 bis 5 beständig ist. Vom Standpunkt des hohen Absorptionsvermögens dieser Lösungen und auf Grund des nach längeren Wellenlängen verschobenen

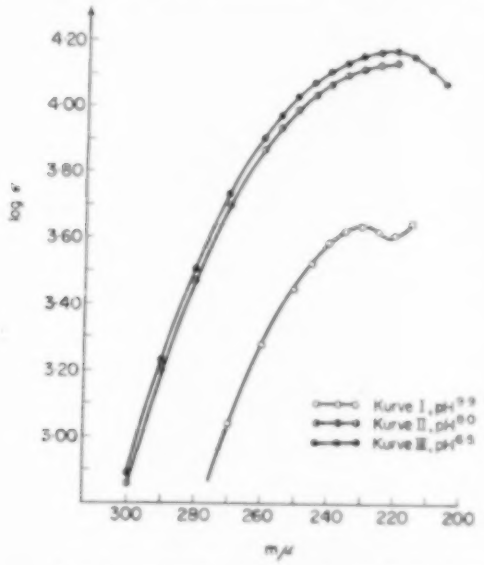

Abb. 2.—Absorptionsspektrum im pH-Gebiet 5–10.

Absorptionsbeginns besteht Veranlassung zu der Annahme, dass in diesem Bereich Niobatteilchen eines höheren Aggregationsgrades vorliegen. Alkaliniobatlösungen mit pH-Werten <5 sind nicht beständig, sondern zersetzen sich unter Abscheidung von $Nb_2O_5 \cdot aq$.

Auf Grund unserer optischen Untersuchungen ist also—in Abhängigkeit vom pH-Wert—die Existenz von drei verschiedenen Anionentypen in Alkaliniobatlösungen wahrscheinlich.

Diffusionsmessungen

Um die bisher gewonnenen Erkenntnisse weiter auszubauen und zu vertiefen, haben wir versucht, die Ionengewichte der drei mutmasslichen Anionentypen zu bestimmen. In der bisher vorliegenden chemischen Literatur sind keine Angaben über Untersuchungen bezüglich des Molekularzustandes von Alkaliniobaten in wässrigen Lösungen enthalten. Für Molekulargewichtsbestimmungen in hydrolysierenden Systemen hat sich die Methode der freien Diffusion ausgezeichnet bewährt;[1] dies trifft besonders für die Ermittlung höherer Teilchengewichte zu. Wir haben uns

[1] G. Jander und K. F. Jahr, *Kolloid-Beihefte* **41**, 1 (1934).

zur Bestimmung der Diffusionsgeschwindigkeit der Methode von OEHOLM[3] bedient, die inzwischen von JANDER und Mitarbeitern[2] modifiziert und verbessert wurde.

In Abb. 3 sind die Ergebnisse unserer Diffusionsversuche in Form der Abhängigkeit der gemessenen spezifischen Diffusionskoeffizienten von den pH-Werten der untersuchten Kaliumniobatlösungen graphisch dargestellt. Daraus geht hervor, dass im relativ stark alkalischen Bereich (pH 11–14) ein Niobatanion existiert, welches—nach der absoluten Grösse des mittleren spezifischen Diffusionskoeffizienten (0·275) zu urteilen—bereits in aggregierter Form vorliegen muss. Es wäre denkbar, dass

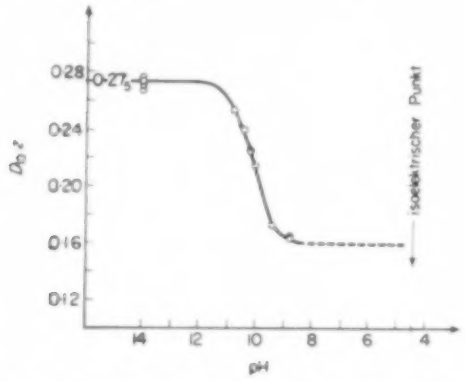

ABB. 3.—Diffusionskoeffizienten in Abhängigkeit vom pH-Wert.

dieses Isopolyniobatanion in extrem alkalischen Lösungen aufgespaltet und vielleicht bis zur monomolekularen Orthoform NbO_4^{3-} abgebaut wird; dieser Vorgang müsste sich durch eine beträchtliche Erhöhung des gemessenen spezifischen Diffusionskoeffizienten kundtun. Diesbezügliche Versuche scheiterten jedoch an der mit zunehmender KOH-Konzentration der Lösungen stark zurückgehenden Löslichkeit von Kaliumniobat. Mit grosser Wahrscheinlichkeit, wenn auch durch Diffusionsmessungen aus gleich zu erörternden Gründen nicht eindeutig beweisbar, ist mit der Existenz eines weiteren hochmolekularen Anionentyps in Alkaliniobatlösungen mit pH-Werten <9 zu rechnen, wie der gestrichelt gezeichnete Teil der Kurve in diesem Gebiet andeuten soll. Die gemessenen D-Werte in der Nähe dieses pH-Wertes zeigen nämlich nicht den monotonen Abfall der bei den etwas höheren pH-Werten ermittelten Diffusionskoeffizienten und lassen daher den Schluss zu, dass die Kurve nicht weiter fällt, sondern dass sich ein neuer Haltepunkt mit $D_{10} \cdot z \simeq 0{\cdot}16$ ausprägt. Leider erwies es sich als unmöglich, für Diffusionsversuche geeignete Niobatlösungen mit pH-Werten <8 herzustellen. Säurezusätze bewirkten eine sofortige irreversible Zersetzung der Niobatlösungen unter $Nb_2O_5 \cdot aq$-Fällung, während durch Einleiten von CO_2 bei Gegenwart der erforderlichen Fremdelektrolytkonzentration (KNO_3) ebenfalls voluminöse weisse Niederschläge entstanden. Überraschenderweise lösten sich letztere beim Verdünnen der Lösungen glatt auf. Eingehendere analytische Untersuchungen* ergaben, dass diese Niederschläge eine definierte Zusammensetzung besitzen, die sie von den aus stärker alkalischen Lösungen kristallisierenden bzw.

* Siehe Teil II: G. JANDER und D. ERTEL, *J. Inorg. Nucl. Chem.* **14**, 77 (1960).

[2] B. GRÜTTNER, G. JANDER und I. BERTRAM, *Z. Anorg. Chem.* **287**, 186 (1956).

[3] W. OEHOLM, *Z. Phys. Chem.* **70**, 378 (1910).

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gefällten Verbindungen deutlich unterscheiden. Daraus ist auf die Existenz eines individuellen Anionentyps in dem in Rede stehenden pH-Bereich zu schliessen, und unsere oben gemachte Annahme wird damit—indirekt— bestätigt.

Durch Anwendung der eingeschränkten RIECKEschen Beziehung[4] $D_1\sqrt{M_1} = D_2\sqrt{M_2}$ und unter Verwendung eines umfangreichen Vergleichsmaterials, das den zahlreichen Untersuchungen von JANDER und Mitarbeitern über Isopolysäuren[1] entnommen ist, gelingt nun die Berechnung der angenäherten Ionengewichte der zur Diskussion stehenden Anionentypen. In Abb. 4 sind die experimentell gemessenen

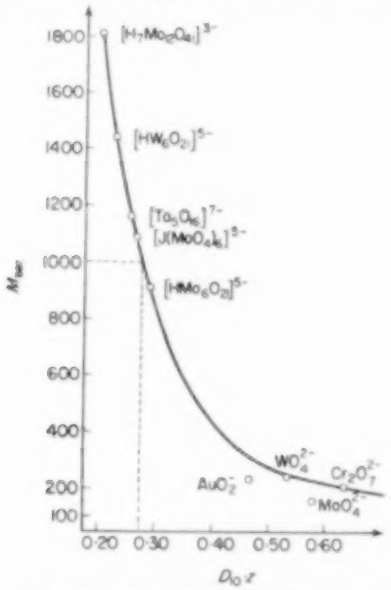

ABB. 4.—Abhängigkeit der spezifischen Diffusionskoeffizienten $D_{10}\cdot z$ vom berechneten Aniongewicht.

spezifischen Diffusionskoeffizienten von verschiedenen Isopolyanionen in Abhängigkeit vom berechneten Ionengewicht eingetragen und durch einen Kurvenzug verbunden. Diese Kurve stellt gewissermassen ein Mittel aller auf der gleichen Grundlage gemessenen D-Werte von verschiedenen, chemisch und konstitutionell jedoch weitgehend ähnlichen Isopolyanionen dar und entspricht deshalb den bei einer Anwendung der RIECKEschen Beziehung zu fordernden Voraussetzungen.[2] Sie gleicht weiterhin unvermeidliche und auf andere Art und Weise vielleicht nicht ohne weiteres aufzudeckende Versuchsfehler aus und ermöglicht daher durch einen einfachen Vergleich aus den von uns gemessenen D-Werten die entsprechenden Ionengewichte mit grösstmöglicher Annäherung und Sicherheit zu ermitteln. Einem mittleren spezifischen Diffusionskoeffizienten $D_{10}\cdot z = 0{\cdot}275$ entspricht nach Abb. 4 ein Ionengewicht von ca. 1000. Setzt man diesen Wert in die eingeschränkte RIECKEsche Beziehung ein, dann resultiert für $D_{10}\cdot z \simeq 0{\cdot}16$ ein Anionengewicht von

$$M = (0{\cdot}275)^2/(0{\cdot}16)^2 \times 1000 \simeq 3000,$$

d.h. annähernd der dreifache Wert.

[4] RIECKE, *Z. Phys. Chem.* **6**, 564 (1890).

Zusammenfassung

Vergleicht man die Ergebnisse unserer Diffusionsversuche mit denjenigen unserer Lichtabsorptionsmessungen, dann sind folgende zusammenfassende Feststellungen zu treffen:

1. Aus den Diffusionsmessungen ergibt sich die Existenz von zwei verschiedenen Aggregationsprodukten, während nach unseren spektrophotometrischen Untersuchungen mit drei Anionentypen im System der Niobisopolysäuren zu rechnen ist.

2. Hinsichtlich des Beständigkeitsbereichs der Teilchen stimmen die Aussagen beider Untersuchungsmethoden insofern überein, als in Alkaliniobatlösungen mit pH-Werten <9 (wahrscheinlich bis in die Nähe des isoelektrischen Punktes[5] bei pH $\sim 4{\cdot}5$) ein definiertes hochmolekulares Hydrolyseprodukt mit einem aus Diffusionsmessungen abgeschätzten Anionengewicht von ca. 3000 vorliegt.

3. Während die Diffusionsmessungen im stark alkalischen Gebiet die Gegenwart nur *eines* definierten Isopolyanions ergeben, ist nach den optischen Untersuchungen im gleichen pH-Bereich mit dem Vorliegen von *zwei* konstitutionell unterschiedlichen Teilchen zu rechnen, die durch einen reversiblen Gleichgewichtszustand miteinander in Beziehung stehen. Aus diesen Feststellungen resultiert die Schlussfolgerung, dass sich die beiden Teilchen gewichtsmässig nicht oder nur sehr wenig voneinander unterscheiden; die Grössenordnung ihrer Ionengewichte beträgt auf Grund unserer Diffusionsversuche ca. 1000.

4. Die Existenz weiterer Anionentypen im System der Niobisopolysäuren—etwa in hochalkalischen Niobatlösungen oder im pH-Bereich 9 bis 11—ist unwahrscheinlich. Lösungsgleichgewichte, deren Einstellung deutlich zeit- oder temperaturabhängig ist, liegen nicht vor.

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EXPERIMENTELLES

Kristallisiertes Kaliumniobat wurde durch Schmelzen von überschüssigem K_2CO_3 oder KOH mit Nb_2O_5, Auflösen des Schmelzkuchens in Wasser und Einengen im Vakuum dargestellt. Natriumniobat erhielten wir als kristalline Fällung beim Versetzen von Kaliumniobatlösungen mit NaOH. Zur Bestimmung des Nb-Gehaltes der Alkalisalze wurden die wässrigen Lösungen mit verd. H_2SO_4 oder mit SO_2 gefällt, die Nb_2O_5·aq-Niederschläge durch Membranfiltration abgetrennt und bei 1000° zu Nb_2O_5 verglüht. Für pH-Messungen verwendeten wir eine Hochalkali-Glaselektrode der Firma Schott und Gen. in Verbindung mit dem pH-Messgerät GM 4491 der Firma Philips bzw. dem Knick-pH-Meter.

Die *Lichtabsorptionsmessungen* wurden mit dem Zeiss-Opton-Spektralphotometer unter Verwendung von Quarzküvetten verschiedener Schichtlänge durchgeführt. Die für die Auswertung der Messergebnisse nach dem Lambert-Beerschen Gesetz erforderlichen Konzentrationsangaben sind auf Mol Nb_2O_5/Liter bezogen. Das Beersche Gesetz ist für Konzentrationen $< 10^{-2}$ Mol Nb_2O_5/Liter erfüllt. Zur Vermeidung von Trübungseffekten wurden alle Lösungen vor den Messungen durch Membran-bzw. Cellafilter filtriert.

Für die *Diffusionsversuche* haben wir uns der von GRÜTTNER, JANDER und BERTRAM[2] angegebenen Arbeitsweise und Apparaturen bedient. Alle Messungen wurden in einem durch elektrische Beheizung auf $19{\cdot}6 \pm 0{\cdot}2°$ temperaturkonstant gehaltenen und weitgehend erschütterungsfreien Kellerraum durchgeführt. Die bei dieser Temperatur ermittelten Diffusionskoeffizienten wurden mit der auf Wasser = 1 bezogenen relativen Zähigkeit z der jeweiligen Überschichtungslösungen multipliziert und aus konventionellen Gründen und Vergleichszwecken mit der von NERNST[6] abgeleiteten Formel $D_t = D_{10}[1 + 0{\cdot}026(t - 10)]$ von $t = 19{\cdot}6°$ auf 10°C umgerechnet.

Die Durchführung dieser Untersuchungen wurde uns durch eine Gewährung von ERP-Mitteln ermöglicht, wofür wir auch an dieser Stelle danken.

[5] D. D. PEIRCE und L. F. YNTEMA, *J. Phys. Chem.* **34**, 1822 (1930).
[6] W. NERNST, *Z. Phys. Chem.* **2**, 613 (1888).

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 77 to 84. Pergamon Press Ltd. Printed in Northern Ireland

ÜBER NIOBSÄUREN UND WASSERLÖSLICHE ALKALINIOBATE—II

PRÄPARATIV-ANALYTISCHE UNTERSUCHUNGEN

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Abstract—The preparation of three types of alkali niobate from niobate solutions with different pH is described; their properties have been examined. All investigated salts are shown as derivatives of a hypothetical hexaniobic acid. The relations between the different isopoly anions are established and discussed. The calculated anionic weights are in good agreement with estimated values from diffusion measurements. By extracting a $NaOH$–Nb_2O_5-melt with absolute ethanol the compound Na_3NbO_4 could be isolated as the most basic sodium niobate. The results of this preparative-analytical investigation confirm and complete the conclusions derived from spectrophotometric and diffusion measurements (cf. Part I*).

IN der älteren chemischen Literatur sind Angaben über die Darstellung von nicht weniger als 15 verschiedenen Alkaliniobattypen zu finden, und bereits dort tauchen immer wieder geäusserte Zweifel bezüglich der Existenz des einen oder anderen Salztyps auf. Unterzieht man diese Literaturangaben einmal einer vergleichenden Betrachtung, dann fällt auf, dass von verschiedenen Autoren unter nahezu gleichen Versuchsbedingungen Salze der unterschiedlichsten Zusammensetzungen erhalten wurden. So soll z.B. nach SANTESSON[1] beim Schmelzen von NaOH mit Nb_2O_5 und Ausziehen des Schmelzkuchens mit Wasser ein Natriumniobat mit einem Molverhältnis $Na_2O : Nb_2O_5 : H_2O$ von 2 : 3 : 9 entstehen. ROSE[2] erhielt dagegen beim Schmelzen von Na_2CO_3 mit Nb_2O_5 und Behandeln dieser Schmelze mit Wasser ein der Zusammensetzung $1 : 1 : x$ entsprechendes Natriumsalz, während nach JÖRGENSEN[2] unter analogen Bedingungen ein $8 : 7 : x$-Salz entsteht und schliesslich BEDFORD[3] eine Verbindung $7 : 6 : x$ fand. Zu (erfolglosen) Versuchen, Natriumsalze der Niobsäure darzustellen, bemerkte MARIGNAC,[4] dass „nur pulverförmige Salze erhalten werden, die beim Waschen ihre Zusammensetzungen verändern und deren keines die Kennzeichen einer ganz bestimmten Verbindung aufwies". Schon aus dieser kurzen Gegenüberstellung wird deutlich, dass die Vielfalt der Ansichten irgendwelchen Versuchsfehlern entspringen muss, seien sie nun fehlerhaften analytischen Bestimmungen, mangelnder Reinheit der Ausgangssubstanzen oder nicht ganz identischen Arbeitsbedingungen zuzuschreiben. Eine neue systematische Bearbeitung dieses Stoffgebietes erscheint daher wünschenswert.

Wir führten zunächst Versuche zur Darstellung von möglichst basenreichem *Kaliumniobat* durch. KOH und Nb_2O_5 wurden in den Molverhältnissen 7 : 1, 14 : 1, 28 : 1 und 60 : 1 in Silbertiegeln so lange geschmolzen, bis eine klare dünnflüssige Schmelze

* G. JANDER und D. ERTEL, *J. Inorg. Nucl. Chem.* **14**, 71 (1960).

[1] B. SANTESSON, *Bull. Soc. Chim. Fr.* [2] **24**, 53 (1875).
[2] H. ROSE und JÖRGENSEN in Gmelin-Kraut, *Handb. Anorg. Chem.* 7. Aufl. Bd. IV, 260 (1928).
[3] M. H. BEDFORD, *J. Amer. Chem. Soc.* **27**, 1216 (1905).
[4] C. MARIGNAC, *Liebigs Ann.* Suppl. Bd. **4**, 273 (1866).

entstanden war. Der nach dem Erkalten grob zerkleinerte Schmelzkuchen wurde in reichlich Wasser—gegebenenfalls unter Erwärmen—gelöst. Die Lösungen liessen wir in hohen Standzylindern ca. 24 Stunden stehen. Dadurch konnten die durch den Angriff von KOH in fein verteilter Form in Lösung gegangenen Silbermengen als schwarze Bodensätze sedimentativ sauber abgetrennt werden. Die abdekantierten und filtrierten Kaliumniobatlösungen engten wir im Vakuum über konz. H_2SO_4 bis zur Kristallisation ein. Die einzeln der Mutterlauge entnommenen Kristalle wurden mehrfach mit destilliertem Wasser abgespült, auf Filtrierpapier oberflächlich getrocknet und bis zur Analyse im Exsikkator über $CaCl_2/CaO$ aufbewahrt.

Die im folgenden angegebenen Analysenergebnisse sind arithmetische Mittelwerte aus jeweils mehreren Einzelbestimmungen. Da für uns eine möglichst genaue Ermittlung der jeweiligen Molverhältnisse $Me_2O : Nb_2O_5$ im Vordergrund des Interesses stand, haben wir von gesonderten H_2O-Bestimmungen abgesehen und verzichten demgemäss auf definitive Angaben bezüglich der Anzahl von Kristallwassermolekeln; es zeigte sich nämlich, dass der Wassergehalt der Salze—je nach Darstellungsart—innerhalb gewisser Grenzen schwanken kann, während die Molverhältnisse $Me_2O : Nb_2O_5$ unabhängig davon stets konstant blieben. Wir deuten deshalb durch das Zeichen „aq" lediglich an, dass die betreffenden Salze hydratisiert vorliegen. Mit der Bezeichnung „aq" bzw. mit der im weiteren Text angewendeten Formelschreibweise für die wasserhaltig kristallisierenden Verbindungen soll auch keine Unterscheidung zwischen möglichen Bindungsarten der H_2O-Molekeln in den Salzen (z.B. Konstitutions- oder Hydratwasser) verbunden sein.

Die analytische Untersuchung der aus den verschiedenen Darstellungsversuchen stammenden Kaliumniobatkristalle ergab in allen Fällen die gleiche Zusammensetzung:

$$K_2O = 28{\cdot}2\,\%$$
$$Nb_2O_5 = 59{\cdot}5\,\%$$
$$H_2O = 12{\cdot}3\,\%$$

Molverhältnis $K_2O : Nb_2O_5 = 1{\cdot}34 : 1$ bzw. $4 : 3$,

Formel: $4\,K_2O{\cdot}3\,Nb_2O_5{\cdot}aq$ bzw. $K_8[Nb_6O_{19}{\cdot}aq]$.

Dieses Kaliumsalz ist also entsprechend dem einfachsten Verhältnis der Molzahlen als Derivat einer Hexaniobsäure zu formulieren. Wir bezeichnen es im folgenden als *Kaliumhexaniobat*(8 : 6), wodurch das Verhältnis Alkaliatome : Niobatome in der Verbindung angedeutet werden soll. Kaliumhexaniobat(8 : 6) kristallisiert in grossen durchsichtigen, häufig büschelförmig zusammengewachsenen Säulen. Seine wässrigen Lösungen reagieren alkalisch; konzentrierte Lösungen weisen pH-Werte von 12–12·5 auf. Verdünnte Mineralsäuren erzeugen in den Lösungen sofort eine Trübung, die sich bei weiterem Säurezusatz verstärkt und schliesslich in eine Fällung von flockigem Niobpentoxydhydrat übergeht. Beim Liegen an der Luft verwittern die Kristalle und werden undurchsichtig, bleiben aber wasserlöslich; das Verwittern geht parallel mit einer Abnahme des Kristallwassergehalts.

Eine andere Möglichkeit zur Darstellung von Kaliumniobat, nämlich der Aufschluss von Nb_2O_5 mit K_2CO_3 bei 1000°, ergab ebenfalls Kristalle mit der analytischen Zusammensetzung des Kaliumhexaniobats(8 : 6).

Ein dritter Weg schliesslich, durch Versetzen wässriger Auflösungen der KOH–Nb_2O_5– oder K_2CO_3–Nb_2O_5–Schmelze mit konz. KOH Kaliumniobat auszufällen, führte zu feinkristallinen Niederschlägen mit etwas höheren Alkaligehalten als dem Kaliumhexaniobat(8 : 6) entsprechen würde. Durch fortgesetztes Auswaschen

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nahmen jedoch die Alkaligehalte allmählich ab und näherten sich schliesslich immer mehr dem Molverhältnis $K_2O : Nb_2O_5 = 1{\cdot}33 : 1$.

Natriumniobat lässt sich leicht durch Versetzen von Kaliumniobatlösungen mit 8–10 n NaOH als schwerlöslicher Niederschlag erhalten. Je nach den Fällungsbedingungen entstehen dabei verschiedenartige Kristallformen. Arbeitet man mit heissen Lösungen, dann bilden sich vorzugsweise säulenförmige, häufig miteinander verwachsene Kristalle der Zusammensetzung

$$Na_2O = 19{\cdot}0\%$$
$$Nb_2O_5 = 61{\cdot}5\%$$
$$H_2O = 19{\cdot}5\%$$

Molverhältnis $Na_2O : Nb_2O_5 = 1{\cdot}33 : 1$ bzw. 4 : 3,
Formel: $4\,Na_2O{\cdot}3\,Nb_2O_5{\cdot}aq$ bzw. $Na_8[Nb_6O_{19}{\cdot}aq]$.

Versetzt man dagegen eiskalte Kaliumniobatlösungen mit eiskalter Natronlauge, dann resultieren flache, tafelförmig-rechteckige Kristalle der Zusammensetzung

$$Na_2O = 18{\cdot}2\%$$
$$Nb_2O_5 = 58{\cdot}7\%$$
$$H_2O = 23{\cdot}1\%$$

Molverhältnis $Na_2O : Nb_2O_5 = 1{\cdot}33 : 1$ bzw. 4 : 3,
Formel: $4\,Na_2O{\cdot}3\,Nb_2O_5{\cdot}aq$ bzw. $Na_8[Nb_6O_{19}{\cdot}aq]$.

Ein Natriumniobat dieser Zusammensetzung, das wir im folgenden als *Natriumhexaniobat*(8 : 6) bezeichnen, ist bisher in der chemischen Literatur nicht erwähnt. Dies ist wahrscheinlich darauf zurückzuführen, dass von anderen Autoren zur Natriumniobatdarstellung fast ausschliesslich ein NaOH– oder Na_2CO_3–Aufschluss von Nb_2O_5 durchgeführt wurde. Wir zeigen weiter unten, dass unter diesen Verhältnissen tatsächlich ein anders zusammengesetztes Natriumsalz entstehen muss.

Natriumhexaniobat(8 : 6) löst sich nur mässig in Wasser; konzentrierte Lösungen haben pH-Werte der Grössenordnung 12. Natronlauge fällt aus den Lösungen wieder Natriumniobat unveränderter Zusammensetzung. Beim Erhitzen auf 1000° spaltet Natriumhexaniobat(8 : 6) Kristallwasser und NaOH ab und geht in unlösliches Natriummetaniobat(1 : 1), $NaNbO_3$, über:

$$Na_8[Nb_6O_{19}{\cdot}x\,H_2O] \rightarrow 6\,NaNbO_3 + 2\,NaOH + (x-1)H_2O.$$

Beim Schmelzen von NaOH oder Na_2CO_3 mit Nb_2O_5 und Auslaugen des zerkleinerten Schmelzkuchens mit Wasser trat wegen der Schwerlöslichkeit von Natriumniobat bei Gegenwart überschüssiger Na^+-Ionen keine Auflösung ein; in Lösung ging lediglich nicht in Reaktion getretenes Natriumhydroxyd bzw. -carbonat. Nach dem Entfernen der Hauptmengen NaOH bzw. Na_2CO_3 kristallisierten wir den Rückstand mehrfach aus Wasser um und erhielten dann prächtige lange Kristallnadeln der Zusammensetzung

$$Na_2O = 16{\cdot}6\%$$
$$Nb_2O_5 = 61{\cdot}3\%$$
$$H_2O = 22{\cdot}1\%$$

Molverhältnis $Na_2O : Nb_2O_5 = 1{\cdot}17 : 1$ bzw. 7 : 6,
Formel: $7\,Na_2O{\cdot}6\,Nb_2O_5{\cdot}aq$ bzw. $Na_7[HNb_6O_{19}{\cdot}aq]$.

Dieses Natriumsalz unterscheidet sich vom Natriumhexaniobat(8 : 6) ausser in seiner Kristallform durch seinen geringeren Alkaligehalt; es ist als saures Salz aufzufassen. Wir bezeichnen diesen Salzytp im folgenden als *Natriumhexaniobat (7 : 6)*. Bezüglich seiner Löslichkeitsverhaltnisse entspricht dieses Salz ungefähr dem Natriumhexaniobat(8 : 6). Beim Erhitzen auf 1000° geht $Na_7[HNb_6O_{19}\cdot aq]$ in $NaNbO_3$ über; der wässrige Auszug des geglühten Salzes reagiert deutlich alkalisch. Die thermische Zersetzung erfolgt also gemäss

$$Na_7[HNb_6O_{19}\cdot x\ H_2O] \rightarrow 6\ NaNbO_3 + NaOH + x\ H_2O.$$

Mit der Zusammensetzung $Na_2O : Nb_2O_5 = 7 : 6$ stimmen die Befunde von LAPITZKI und SPITZYN[5], sowie von SUE[6] überein. Die Aufstellung der Formel $Na_7[HNb_6O_{19}\cdot aq]$ erfolgte in Anlehnung an die Resultate einer röntgenographischen Untersuchung von LINDQUIST[7], der im Natriumsalz $7\ Na_2O\cdot 6\ Nb_2O_5\cdot 32\ H_2O$ die Existenz der Gruppe $[Nb_6O_{19}]^{8-}$ als Strukturelement nachgewiesen hat, wobei H_2O-Molekeln als „Sauerstofflieferanten"—vermutlich in Form von Hydroxylgruppen—fungieren.

Welche Beziehungen bestehen nun zwischen den beiden Salztypen $Na_8[Nb_6O_{19}\cdot aq]$ und $Na_7[HNb_6O_{19}\cdot aq]$? Bezüglich der Entstehungsbedingungen ist festzustellen, dass Natriumhexaniobat(8 : 6) stets aus stark alkalischen Lösungen kristallisiert, während Natriumhexaniobat(7 : 6) infolge der besonderen Löslichkeitsverhältnisse beim NaOH- bzw. Na_2CO_3-Aufschluss von Nb_2O_5 erst dann isoliert werden konnte, als der Alkaliüberschuss entfernt worden war, d.h. es bildet sich im weniger alkalischen Medium. Aus Lichtabsorptions- und Diffusionsmessungen an Alkaliniobatlösungen* schlossen wir im pH-Gebiet 10–14 auf die Existenz eines reversiblen Gleichgewichts zwischen zwei Anionentypen, die sich zwar konstitutionell, nicht aber hinsichtlich ihrer Teilchengewichte voneinander unterscheiden. Wir formulieren daher:

$$[Nb_6O_{19}\cdot aq]^{8-} \underset{OH^-}{\overset{H^+}{\rightleftarrows}} [HNb_6O_{19}\cdot aq]^{7-},$$

wobei der Umwandlungspunkt auf Grund unserer UV-spektrophotometrischen Untersuchungen bei pH ~ 13 liegt. Aus dieser Überlegung folgt, dass in wässrigen Lösungen von Natrium- oder Kaliumhexaniobat(8 : 6) keine $[Nb_6O_{19}\cdot aq]^{8-}$-Ionen vorliegen (selbst konzentrierte Lösungen weisen ja nur pH-Werte um 12 auf), sondern dass bereits $[HNb_6O_{19}\cdot aq]^{7-}$-Ionen entstanden sein müssen. Dies konnten wir beweisen, indem sich das Salz $Na_8[Nb_6O_{19}\cdot aq]$ durch Umkristallisieren ohne weiteres in $Na_7[HNb_6O_{19}\cdot aq]$ überführen liess, und indem aus Alkalihexaniobat(8 : 6)-Lösungen mit pH-Werten 11–12 auf Zugabe wasserlöslicher organischer Lösungsmittel (Methanol, Äthanol, Aceton usw.) feinkristalline Alkalihexaniobat(7 : 6) ausfielen. Anderserseits konnte durch Einfliessenlassen einer Natriumhexaniobat-(7 : 6)-Lösung in starke Natronlauge kristallines $Na_8[Nb_6O_{19}\cdot aq]$ erhalten werden. In einem Modell-versuch konnten wir ferner nachweisen, dass eine Umwandlung $Na_8[Nb_6O_{19}\cdot aq] \rightarrow Na_7[HNb_6O_{19}\cdot aq]$ auch in fester Phase möglich ist. Wir suspendierten $Na_8[Nb_6O_{19}\cdot aq]$ in einer 1 m $NaClO_4$-Lösung unter Rühren und stellten—obwohl

* Siehe Teil I: G. JANDER und D. ERTEL, *J. Inorg. Nucl. Chem.* **14**, 71 (1960).

[5] A. W. LAPITZKI und V. I. SPITZYN, *J. Allg. Chem.* (*Russ.*) **1**, 37 (1953); *J. Angew. Chem.* (*Russ.*) **26**, 101 (1953).

[6] P. SÜE, *Ann. Chim.* [11] **7**, 493 (1937).

[7] I. LINDQUIST, *Arkiv Kemi* **5**, 247 (1952).

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sich das Natriumniobat in diesem Medium nicht auflösen kann—eine allmähliche Umwandlung in das (7 : 6)-Salz fest. Wir sind deshalb der Überzeugung, dass das primäre Hydrolyseprodukt der NaOH—Nb_2O_5-Schmelze Natriumhexaniobat (8 : 6) ist. Die obenstehende Gleichgewichtsformulierung entspricht auch den Resultaten unserer Diffusionsmessungen, indem sich beide Teilchen gewichtmässig nur ganz unwesentlich voneinander unterscheiden. Wir hatten aus unseren Untersuchungen ein Ionengewicht von ca. 1000 ermittelt, das mit den errechneten Anionengewichten von $[Nb_6O_{19}]^{8-} = 862$ und $[HNb_6O_{19}]^{7-} = 863$ grössenordnungsmässig übereinstimmt. Zieht man in Betracht, dass die diffundierenden Ionen sicher von mitwandernden Hydrathüllen eingeschlossen sind, die bei der Ionengewichtsbestimmung mit eingehen, sich aber quantitativ kaum in Rechnung stellen lassen, dann wird die Übereinstimmung der Ergebnisse noch besser.

Auf Grund der Resultate unserer Lichtabsorptions- und Diffusionsmessungen sollte in ganz schwach alkalischen Niobatlösungen (pH < 9) ein weiterer Anionentyp beständig sein, dessen Existenz nun durch die präparative Darstellung entsprechender Salze zu beweisen ist. Die Darstellung eines solchen Kaliumsalzes gelang uns auf folgendem Wege: 3–4 prozentige Lösungen von Kaliumhexaniobat(8 : 6) wurden unter äusserer Kühlung mit Eis und kräftigem mechanischen Rühren tropfenweise mit Methylalkohol versetzt. Als etwa die Hälfte des Volumens der wässrigen Lösungen an Methanol zugesetzt worden war, setzte eine Fällung von weissen, flockigen und bei mikroskopischer Betrachtung amorph erscheinenden Niederschlägen ein; nach Zugabe eines äquivalenten Volumens Methylalkohol war die Fällung praktisch vollständig. Die Flocken setzten sich gut ab und waren leicht abzufiltrieren. Die Niederschläge wurden zunächst mit verdünntem (50%), dann mit reinem Alkohol gut ausgewaschen und im Vakuum über konz. H_2SO_4 getrocknet; während des Trockenvorgangs trat eine erhebliche Schrumpfung ein. Die Substanzen hatten folgende Zusammensetzung:

$$K_2O = 23{\cdot}6\%$$

$$Nb_2O_5 = 65{\cdot}9\%$$

$$H_2O = 10{\cdot}5\%$$

Molverhältnis $K_2O : Nb_2O_5 = 1{\cdot}01 : 1$
Formel: $K_2O{\cdot}Nb_2O_5{\cdot}aq$ bzw. $KNbO_3{\cdot}aq$.

Wurde das Waschen mit reinem Methylalkohol weggelassen, im übrigen aber wie oben verfahren, erhielten wir Verbindungen der Zusammensetzung:

$$K_2O = 21{\cdot}2\%$$

$$Nb_2O_5 = 59{\cdot}8\%$$

$$H_2O = 19{\cdot}0\%$$

Molverhältnis $K_2O : Nb_2O_5 = 1{\cdot}00 : 1$,
Formel: $K_2O{\cdot}Nb_2O_5{\cdot}aq$ bzw. $KNbO_3{\cdot}aq$.

Beide Verbindungen unterscheiden sich also nur in ihrem Wassergehalt, sind aber sonst analog zusammengesetzt und als *hydratisiertes Kaliummetaniobat* zu bezeichnen. Wir möchten an dieser Stelle darauf hinweisen, dass die bei den Versuchen zur

Herstellung ganz schwach alkalischer Diffusionslösungen* (pH < 8) stets aufgetretenen Niederschläge bezüglich ihrer Zusammensetzungen mit dem hier beschriebenen hydratisierten Kaliummetaniobat identisch sind. Die durch gleichionige Zusätze in der für Diffusionsversuche erforderlichen Konzentrationsgrössenordnung hervorgerufene relativ starke Löslichkeitserniedrigung von hydratisiertem Metaniobat scheint charakteristisch für diesen Salztyp zu sein.

Die Formulierung des hydratisierten Kaliummetaniobats als $KNbO_3 \cdot aq$ ist eine Vereinfachung, die den Resultaten unserer Diffusions- und Lichtabsorptionsmessungen nicht gerecht wird. Aus den im folgenden genannten Gründen halten wir die Formel $(K_6[Nb_6O_{18} \cdot aq])_n$ für zutreffend:

1. Nach allen Erfahrungen auf dem Gebiet der Isopolysäuren findet mit zunehmender Wasserstoffionenkonzentration stets eine fortschreitende Aggregation, niemals aber eine Aufspaltung bereits vorhandener stabiler Aggregationsprodukte in Teilchen mit einem kleineren Kondensationsgrad statt.
2. Die äusserlich amorph erscheinende Form, in der das Metaniobat im Gegensatz zu den beiden Hexaniobaten aus den Lösungen ausfällt, macht das Vorliegen eines relativ hohen Molekulargewichts wahrscheinlich. Wir formulieren deshalb das Metaniobat als Salz der Hexaniobsäure und deuten durch den Index *n* den polymeren Charakter dieser Verbindung an.
3. Hydratisiertes Metaniobat entsteht aus Hexaniobat(7 : 6), mit dem es in einem reversiblen Gleichgewichtszustand steht:

$$n[HNb_6O_{19} \cdot aq]^{7-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [Nb_6O_{18} \cdot aq]_n^{6-},$$

wobei der Umwandlungspunkt auf Grund unserer optischen Untersuchungen bei pH ~ 9 liegt.

Das Metaniobatanion müsste nach unseren Diffusionsmessungen ein Ionengewicht von ca. 3000 haben. Aus der Formel $[Nb_6O_{18}]^{6-}$ errechnet sich ein Gewicht von 845. Dem Index *n* entspricht daher ein zwischen den Zahlen 3 und 4 liegender Wert, wobei beachtet werden muss, dass bei der Berechnung des Anionengewichts das Gewicht einer etwa vorhandenen Wasserhülle nicht mit erfasst wurde, während ein solches im gefundenen Ionengewicht von ca. 3000 mit enthalten ist. Das berechnete Anionengewicht 845 stellt also gewissermassen einen Mindestwert dar. Die Formulierung $[Nb_6O_{18} \cdot aq]_3^{6-}$ dürfte deshalb den tatsächlich vorliegenden Verhältnissen am besten gerecht werden. Wir werden im folgenden diesen Anionentyp als *Hexametaniobat*(6 : 6) bezeichnen.

Kaliumhexametaniobat(6 : 6) ist etwas hygroskopisch und löst sich leicht in Wasser; die Lösungen reagieren neutral. Beim Erhitzen auf 1000° geht Kaliumhexametaniobat(6 : 6) in unlösliches, wasserfreies Kaliummetaniobat(1 : 1) über:

$$K_6[Nb_6O_{18} \cdot x\,H_2O] \rightarrow 6\,KNbO_3 + x\,H_2O.$$

Der wässrige Auszug des geglühten Salzes reagiert neutral. Durch dieses Verhalten unterscheidet sich das Hexametaniobat(6 : 6) charakteristisch von den Alkalihexaniobaten(8 : 6) und —(7 : 6).

* Siehe Teil I: G. JANDER und D. ERTEL, *J. Inorg. Nucl. Chem.* **14**, 71 (1960).

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Zur Vervollständigung des aufzustellenden Hydrolyseschemas haben wir uns auch mit der Darstellung und Untersuchung von *Natriumorthoniobat* befasst. LAPITZKI und SPITZYN[5] haben durch Schmelzen von NaOH mit Nb_2O_5 und Extraktion des überschüssigen Hydroxyds mit absolutem Alkohol die Verbindung Na_5NbO_5 dargestellt. Deren Existenz konnte jedoch von REISMAN, HOLTZBERG und BANKS[8] auf Grund differentialthermoanalytischer Untersuchungen am System Na_2O–Nb_2O_5 nicht bestätigt werden; die höchstbasische Verbindung soll nach diesen Autoren die Zusammensetzung Na_3NbO_4 besitzen. Bei unseren Darstellungsversuchung hielten wir uns im Prinzip an die von LAPITZKI und SPITZYN empfohlene Arbeitsweise. Wir arbeiteten mit molaren Mischungsverhältnissen NaOH : Nb_2O_5 = 20 : 1 bis 40 : 1 bei Temperaturen zwischen 450° und 850° und einer Schmelzdauer von 1–7 Stunden. Das Resultat dieser Darstellungsversuche war in allen Fällen eine schwach gelblich gefärbte, sandartig kristalline, schwere Substanz folgender Zusammensetzung:

$$Na_2O = 41{\cdot}23\%$$
$$Nb_2O_5 = 58{\cdot}72\%$$

Molverhältnis $Na_2O : Nb_2O_5 = 3{\cdot}01 : 1$,
Formel: $3\,Na_2O{\cdot}Nb_2O_5$ bzw. Na_3NbO_4.

Wir bezeichnen diese Verbindung im folgenden als *Natriumorthoniobat*(3 : 1). Na_3NbO_4 löst sich mit stark alkalischer Reaktion in Wasser; anfangs ist dabei eine schwache, jedoch bald wieder verschwindende Trübung zu beobachten. Beim Einengen dieser Lösungen scheidet sich kristallines Natriumhexaniobat(8 : 6) ab. Eine rückläufige Umwandlung Hexaniobat(8 : 6) → Orthoniobat(3 : 1) wurde von uns in wässrigen Lösungen niemals beobachtet. Wir nehmen daher bei Einwirkung von Wasser auf Na_3NbO_4 folgende irreversible Hydrolysereaktion an

$$6\,Na_3NbO_4 + (x + 5)\,H_2O \rightarrow Na_8[Nb_6O_{19}{\cdot}x\,H_2O] + 10\,NaOH.$$

Beim Erhitzen auf 1000° schmilzt Na_3NbO_4 ohne Zersetzungserscheinumgen.

Bei unseren Darstellungsversuchen konnten wir in keinem Fall eine Verbindung isolieren, deren Zusammensetzung auch nur annähernd der von Na_5NbO_5 entsprochen hätte. Immerhin wäre es jedoch denkbar, dass der zur Extraktion von NaOH verwendete absolute Äthylalkohol auf vielleicht entstandenes Na_5NbO_5 solvolytisch einwirkt, und dass wir deshalb immer das Solvolyseprodukt Na_3NbO_4 erhalten haben. Wir führten aus diesem Grunde auch Extraktionsversuche mit absolutem n-Propylalkohol und n-Butylalkohol durch. Da sich jedoch die Zusammensetzung der Extraktionsrückstände nicht änderte, müssen wir die Existenz des von LAPITZKI und SPITZYN in gleicher Weise dargestellten Natriumorthoniobats(5 : 1), Na_5NbO_5, bezweifeln. Bei Verwendung von absolutem Methylalkohol als Extraktionsmittel beobachteten wir dagegen eine langsame Solvolysereaktion, deren Endprodukt das in Wasser unlösliche Natriummetaniobat(1 : 1), $NaNbO_3$, ist.

Zusammenfassung.

Unsere präparativ-analytischen Untersuchungen ergaben—in Abhängigkeit vom pH-Wert der Niobatlösungen—die Existenz von drei verschiedenen Isopolyniobatanionen. Das bisher noch unbekannte Natriumhexaniobat(8 : 6), $Na_8[Nb_6O_{19}{\cdot}aq]$,

[8] A. REISMAN, F. HOLTZBERG und E. BANKS, *J. Amer. Chem. Soc.* **80**, 37 (1958).

konnte durch doppelte Umsetzungen von Kaliumhexaniobat(8 : 6)-Lösungen mit NaOH dargestellt werden. Beim Aufschluss von Nb_2O_5 mit NaOH oder Na_2CO_3 entsteht nach dem Auslaugen der Schmelze mit Wasser infolge der besonderen Löslichkeitsverhältnisse die Verbindung $Na_7[HNb_6O_{19}\cdot aq]$, die als Hydrolyseprodukt des primär entstandenen Natriumsalzes $Na_8[Nb_6O_{19}\cdot aq]$ aufzufassen ist. Verbindungen mit dem Anion $[HNb_6O_{19}\cdot aq]^{7-}$ lassen sich auch durch Umkristallisieren von Alkalihexaniobaten(8 : 6) aus Wasser, sowie durch Fällung nicht zu verdünnter Alkalihexaniobat(8 : 6)-Lösungen mit wasserlöslichen organischen Solventien erhalten. Bei der Fällung stark verdünnter Hexaniobatlösungen mit Methylalkohol entstehen hochaggregierte Hexametaniobate(6 : 6), $[Nb_6O_{18}\cdot aq]_n^{6-}$. Die Beziehungen zwischen den verschiedenen Isopolyniobaten lassen sich durch folgende schematische Reaktionsgleichungen beschreiben:

$$[Nb_6O_{19}\cdot aq]^{8-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [HNb_6O_{19}\cdot aq]^{7-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [Nb_6O_{18}\cdot aq]_n^{6-}.$$

Die Existenzbereiche dieser Isopolyanionen sind untereinander durch reversible Gleichgewichtszustände verbunden. Der Übergang $[Nb_6O_{19}\cdot aq]^{8-} \rightleftarrows [HNb_6O_{19}\cdot aq]^{7-}$ vollzieht sich bei pH ~ 13, der von $[HNb_6O_{19}\cdot aq]^{7-}$ nach $[Nb_6O_{18}\cdot aq]_n^{6-}$ bei pH ~ 9. Die auf Grund dieser Formulierungen berechneten Ionengewichte befinden sich in guter Übereinstimmung mit den Ergebnissen unserer Diffusionsversuche. Aus der Schmelze des NaOH—Nb_2O_5—Aufschlusses konnte als höchstbasisches Natriumniobat die Verbindung Na_3NbO_4 isoliert werden. Bei Einwirkung von Wasser auf Na_3NbO_4 bildet sich in einer irreversiblen Hydrolysereaktion Natriumhexaniobat(8 : 6), während beim Kochen von Na_3NbO_4 mit absolutem Methylalkohol eine langsame Solvolyse zu $NaNbO_3$ stattfindet.

Die Resultate unserer präparativ-analytischen Untersuchungen bestätigen und ergänzen also die aus den Lichtabsorptions- und Diffusionsmessungen gezogenen Schlussfolgerungen.

EXPERIMENTELLES

Zur Darstellung der Niobate wurden Chemikalien höchster Reinheit (p.a. von MERCK) verwendet. Das Niobpentoxyd hatte eine überprüfte Reinheit von 99·5 Prozent (0·3% SiO_2). Die Aufschlüsse wurden in Silber- bzw. Platintiegeln durchgeführt. Die analytische Untersuchung der Alkaliniobate erfolgte hauptsächlich so, dass die in Wasser gelöste Einwaage (ca. 0·5 g) bei ca. 80° unter Rühren mit einer genau bekannten Menge 0,1 n $HClO_4$ oder H_2SO_4 im Überschuss versetzt wurde. Nach dem Abfiltrieren des quantitativ ausgefallenen Niobpentoxydhydrats durch Membranfilter, Überführen in einen gewogenen Platintiegel und Verglühen bei 1000° zu Nb_2O_5, wurde im Filtrat die überschüssige Säure mit 0·1 n NaOH zurücktitriert und aus dem effektiven Säureverbrauch der Alkaligehalt berechnet. In einzelnen Fällen wurde die Alkalibestimmung in den Filtraten der Niobpentoxydhydratniederschläge auch durch Ionenaustausch durchgeführt; als Austauscher verwendeten wir Permutit ES in der OH-Form. Den Kristallwassergehalt der Alkaliniobate ermittelten wir durch Ergänzung der gefundenen Prozentzahlen für Nb_2O_5 und Me_2O zu 100. Nur in einzelnen Fällen führten wir zur Kontrolle auch Bestimmungen des Glühverlustes der Salze durch. Die in Wasser unlöslichen Alkalimetaniobate, $MeNbO_3$, wurden durch Aufschliessen mit $KHSO_4$ oder K_2CO_3, Lösen der Schmelze in Wasser und Versetzen der siedenden Lösungen mit NH_4OH bzw. verdünnter Schwefelsäure—wobei $Nb_2O_5\cdot aq$ quantitativ abgeschieden wird-analysiert.

Die Durchführung dieser Untersuchungen wurde uns durch eine Gewährung von ERP-Mitteln ermöglicht, wofür wir auch an dieser Stelle danken.

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ÜBER NIOBSÄUREN UND WASSERLÖSLICHE ALKALINIOBATE—III

KONDUKTOMETRISCHE TITRATIONEN UND VERGLEICHENDE RÖNTGENOGRAPHISCHE UNTERSUCHUNGEN. DAS HYDROLYSESCHEMA DER ISOPOLYNIOBATE

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Abstract—Conductometric titrations of aqueous solutions of alkali niobates with diluted mineral acids and X-ray studies of the different salts complete and confirm the results on of chemistry of isopoly niobates hitherto obtained.

A graphic scheme of hydrolytic reactions in solutions of alkali niobates is presented and explained by a short over-all summary of the work.

Konduktometrische Titrationen

Um das mit Hilfe der bereits besprochenen Untersuchungsmethoden* entwickelte Bild der in Alkaliniobatlösungen vorliegenden Hydrolysegleichgewichte abzurunden und gegebenenfalls zu vervollständigen, haben wir Lösungen der verschiedenen Alkaliniobate mit verdünnten Mineralsäuren konduktometrisch titriert. Die jeweils bei bestimmten Molverhältnissen von zugesetzter Säure zu vorgelegtem Alkaliniobat auftretenden Leitfähigkeitsänderungen stehen mit dem Chemismus der Hydrolysevorgänge unmittelbar in Beziehung und vermitteln deshalb einen Einblick in die im Gesamtverlauf einer Titration sich abspielenden Reaktionen.

Über elektrometrische Untersuchungen von Alkaliniobatlösungen sind in der chemischen Literatur einige Angaben enthalten. BRITTON und ROBINSON[1], PEIRCE und YNTEMA[2], sowie SÜE[3] berichteten bereits über konduktometrische bzw. potentiometrische Titrationen, beschäftigten sich aber immer nur mit einem Salztyp. Unsere Untersuchungen bestätigen zwar im wesentlichen die Ergebnisse dieser Autoren, doch dürfte eine Zusammenstellung des Verhaltens der verschiedenen von uns dargestellten Salztypen aus Übersichts- und Vergleichszwecken von Interesse sein.

In den Abb. 1–4 ist der Verlauf der konduktometrischen Titration wässriger Lösungen von Na_3NbO_4, $Na_8[Nb_6O_{19}\cdot aq]$, $Na_7[HNb_6O_{19}\cdot aq]$ und $(K_6[Nb_6O_{18}\cdot aq])_3$ mit verdünnter $HClO_4$ bzw. H_2SO_4 graphisch dargestellt. Aus einer vergleichenden Betrachtung ergeben sich folgende Gesichtspunkte: Der zunächst stattfindenden Neutralisation von hydrolytisch gebildeten OH^--Ionen schliesst sich bei nur relativ geringen Leitfähigkeitsänderungen die Zersetzung der Alkaliniobatlösungen unter Abscheidung von $Nb_2O_5\cdot aq$ an, und schliesslich nimmt die Leitfähigkeit durch überschüssige

* Siehe Teil I und II: G. JANDER und D. ERTEL, *J. Inorg. Nucl. Chem.* **14**, 71, 77 (1960)

[1] H. T. S. BRITTON und R. A. ROBINSON, *J. Chem. Soc.* 2265 (1932).
[2] D. D. PEIRCE und L. F. YNTEMA, *J. Phys. Chem.* **34**, 1822 (1930).
[3] P. SÜE, *Ann. Chim.* [11] **7**, 493 (1937).

freie Säure stark zu. Je höher basisch das untersuchte Niobat ist, desto länger ist der abfallende Kurvenast; die Neutralisation freier Hydroxylionen ist stets dann beendet, wenn der Alkaligehalt der in Lösung befindlichen Niobate dem der Zusammensetzung

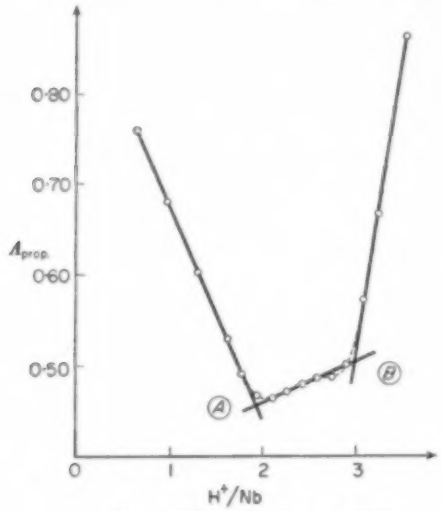

ABB. 1.—Na_3NbO_4—0·1 n $HClO_4$.

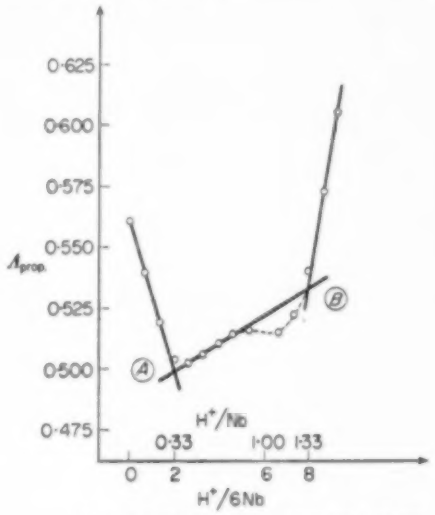

ABB. 2.—$Na_8[Nb_6O_{19}.aq]$—0·121 n H_2SO_4.

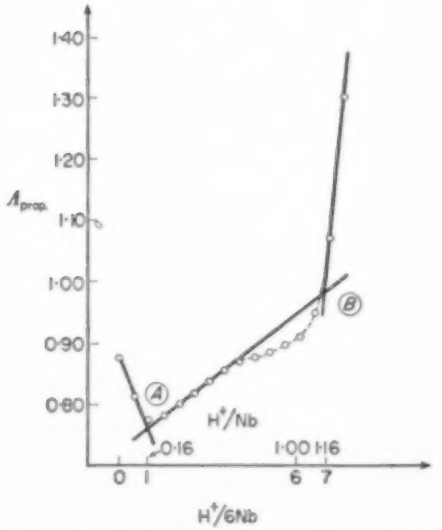

ABB. 3.—$Na_7[HNb_6O_{19}.aq]$—0·1 n $HClO_4$.

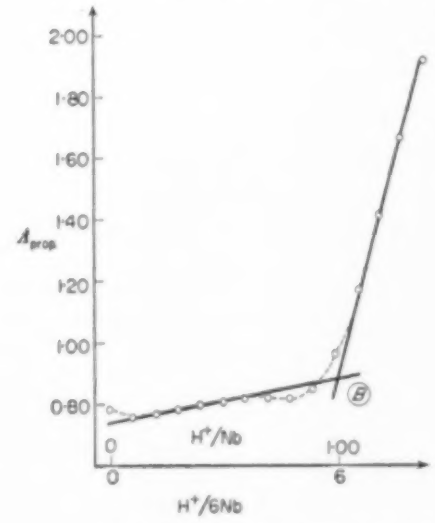

ABB. 4.—$K_8[Nb_6O_{19}.aq]$—0·1 n $HClO_4$.

$Me_8[Nb_6O_{18}.aq]$ (Me = Alkaliatom) entspricht (vgl. Punkte A). Bei den jeweils gestrichelt gezeichneten Teilen der Titrationskurven—kurz vor Erreichen der Äquivalenzpunkte B—waren die Leitfähigkeitswerte nicht konstant, wahrscheinlich wegen der adsorptiven Eigenschaften des in diesem Gebiet ausfallenden Niobpentoxydhydrats.

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Bevor wir auf die Einzelreaktionen bei den Titrationen eingehen, wollen wir eine Übersicht über die auf Grund der bisherigen Untersuchungsergebnisse feststehenden Teilreaktionen des gesamten Hydrolysevorganges in Alkaliniobatlösungen geben: Beim Auflösen von Orthoniobat (3 : 1) erfolgt primär Bildung von Hexaniobat (8 : 6), welches bei allmählich steigender Wasserstoffionenkonzentration zunächst in Hexaniobat (7 : 6) und schliesslich in Hexametaniobat (6 : 6) übergeht. Letzteres wird durch überschüssiges Säure unter Abscheidung von $Nb_2O_5 \cdot aq$ zersetzt. Die Teilreaktionen dieses Gesamtverlaufs sind:

$$6NbO_4^{3-} + 10H^+ \rightarrow [Nb_6O_{19} \cdot aq]^{8-} + 5H_2O \qquad \text{I}$$

$$[Nb_6O_{19} \cdot aq]^{8-} + H^+ \rightleftharpoons [HNb_6O_{19} \cdot aq]^{7-} \qquad (p_H \sim 13)\ \text{II}$$

$$[HNb_6O_{19} \cdot aq]^{7-} + H^+ \rightleftharpoons [Nb_6O_{18} \cdot aq]^{6-} + H_2O \qquad (p_H \sim 9)\ \text{III}$$

$$[Nb_6O_{18} \cdot aq]^{6-} + 6H^+ \rightarrow H_6[Nb_6O_{18} \cdot aq] \rightarrow 3Nb_2O_5 \cdot aq + 3H_2O \qquad \text{IV}$$

$$\Sigma\ \text{I–IV}: \quad 6NbO_4^{3-} + 18H^+ \rightarrow 3Nb_2O_5 \cdot aq + 9H_2O$$

Abbildung 1. Titration von Na_3NbO_4 mit 0·1 n $HClO_4$. Knickpunkt A liegt bei $2H^+$/Nb bzw. $12H^+$/6 Nb; der abfallende Kurvenast entspricht also dem Ablauf der Teilreaktionen I–III. Dass sich die Einzelreaktionen nicht durch besondere Knickpunkte bemerkbar machen, erklärt sich dadurch, dass die Reaktion I beim Auflösen von Na_3NbO_4 praktisch sofort und irreversibel von links nach rechts abläuft, und dass die bei $p_H \sim 13$ stattfindende Reaktion II wegen der hohen Hydroxylionenkonzentration und der dadurch bedingten beträchtlichen Leitfähigkeit konduktometrisch nicht erfasst werden kann.—Der Säureverbrauch zwischen A und B beträgt 1 H^+/Nb bzw. $6H^+$/6 Nb; dieser Teil der Kurve charakterisiert den Ablauf der Teilreaktion IV. Der Äquivalenzpunkt B liegt bei $3H^+$/Nb und entspricht damit—im ganzen gesehen—dem Ersatz sämtlicher Na^+-Ionen im Na_3NbO_4 durch H^+-Ionen.

Abbildung 2. Titration von $Na_8[Nb_6O_{19} \cdot aq]$ mit 0·121 n H_2SO_4. Knickpunkt A liegt bei $2H^+$/6 Nb, zeigt also den Ablauf der Teilreaktionen II und III an. Der Grund dafür, dass sich die Reaktion II auch hier nicht durch eine entsprechende Leitfähigkeitsänderung bemerkbar macht, ist darin zu suchen, dass in der vorgelegten Niobatlösung (pH ~ 11) gar kein Hexaniobat (8 : 6), $[Nb_6O_{19} \cdot aq]^{8-}$ mehr vorliegt, sondern dass sich bereits Hexaniobat (7 : 6), $[HNb_6O_{19} \cdot aq]^{7-}$, durch Hydrolyse gebildet hat.* Die ursprüngliche Anwesenheit von Hexaniobat (8 : 6) gibt sich lediglich noch durch das pro Mol Hexaniobat (8 : 6) entstandene OH^--Äquivalent zu erkennen. Die Differenz des Säureverbrauchs zwischen B und A beträgt auch in diesem Fall $6H^+$/6 Nb und entspricht deshalb der Teilreaktion IV.

Abbildung 3. Titration von $Na_7[HNb_6O_{19} \cdot aq]$ mit 0·1 n $HClO_4$. Knickpunkt A ($1H^+$/6Nb) entspricht dem vollständigen Ablauf der Teilreaktion III, Knickpunkt B ($6H^+$/6 Nb) dem der Teilreaktion IV.

Abbildung 4. Titration von $(K_6[Nb_6O_{18} \cdot aq])_3$ mit 0·1 n $HClO_4$. Durch Hydrolyse entstandene OH^--Ionen sind hier nicht vorhanden. Die Titration beginnt vielmehr gleich in dem Stadium, das bei den anderen Titrationen erst nach Neutralisation der hydrolytisch gebildeten Hydroxylionen erreicht war (vgl. Punkte A). Der Säureverbrauch bis zum Äquivalenzpunkt B beträgt $6H^+$/6 Nb und entspricht damit der Teilreaktion IV.

* Siehe Teil II: G. Jander und D. Ertel, *J. Inorg. Nucl. Chem.* **14**, 77 (1960).

Wir stellen zusammenfassend fest, dass unsere konduktometrischen Untersuchungen von Alkaliniobatlösungen die Ergebnisse der vorangegangenen Untersuchungsmethoden vollauf bestätigen.

Vergleichende röntgenographische Untersuchungen

Um festzustellen, ob und inwieweit sich die verschiedenen von uns dargestellten Alkaliniobate im festen Zustand strukturell voneinander unterscheiden, haben wir Debye–Scherrer Aufnahmen von je einem Salztyp hergestellt. Ausserdem wurden die Änderungen verfolgt, die sich nach dem Erhitzen der Verbindungen auf 1000° in den Debyeogrammen abzeichneten.—Wir fanden, dass die Hexaniobate (8 : 6), (7 : 6) und (6 : 6) unterschiedliche, jedoch für jeden Verbindungstyp charakteristische Debye–Scherrer Diagramme lieferten, wobei aus dem Linienreichtum und dem im ganzen gesehen wenig ausgeprägten Charakter der Debyeogramme auf das Vorliegen komplizierter Strukturen mit geringer Symmetrie zu schliessen ist.—Nach Erhitzen der Hexaniobate (8 : 6), (7 : 6) und (6 : 6) wurden untereinander identische Röntgendiagramme mit relativ wenigen, dafür um so prägnanteren Linien erhalten. Dies ist auf die Bildung entsprechender Metaniobate (1 : 1), $MeNbO_3$, zurückzuführen, deren kubische Struktur bekannt ist.[4] Damit konnten die aus den Ergebnissen anderer Untersuchungsmethoden gezogenen Schlussfolgerungen bezüglich des thermischen Verhaltens der Alkalihexaniobate röntgenographisch bestätigt werden. Na_3NbO_4 unterscheidet sich durch sein Röntgendiagramm deutlich von den vorstehend beschriebenen Verbindungen; nach Erhitzen auf 1000° änderte sich das Diagramm nicht.

EXPERIMENTELLES

Die *Leitfähigkeitstitrationen* führten wir bei Raumtemperatur mit einer Messapparatur der Firma Ruhstrat, Göttingen, nach der visuellen Kompensationsmethode durch. Wir arbeiteten mit Halbmikrobüretten; während der Titration wurde die Messlösung lebhaft gerührt. Die Relationen Säure: Alkaliniobat wurden in Molverhältnisse H^+/Nb bzw. H^+/6 Nb umgerechnet, indem wir die eingewogene Niobatmenge auf Grund des analytisch ermittelten Nb_2O_5-Gehaltes als Grammatome Nb in Rechnung stellten.

Die *Debye–Scherrer Aufnahmen* wurden unter Verwendung von Cu $K\alpha$-Strahlung (Ni Filter) in einer Röntgenkamera mit 57·3 mm Durchmesser hergestellt. Die Belichtungszeiten betrugen 0·5 bis 1·5 Stunden.

Das Hydrolyseschema der Isopolyniobate

In Abb. 5 haben wir versucht, sämtliche wesentlichen Versuchsergebnisse unserer Untersuchungen über Niobsäuren und wasserlösliche Alkaliniobate übersichtlich zusammenzustellen und die zwischen den einzelnen Salztypen vorliegenden Beziehungen zum Ausdruck zu bringen. Die folgende kurze Zusammenfassung unserer Arbeit soll zur Erläuterung des Schemas dienen.

Durch *Lichtabsorptionsmessungen** konnte die Existenz von drei Anionentypen in Alkaliniobatlösungen mit pH-Werten 5–14 nachgewiesen werden. Die Beständigkeitsbereiche dieser miteinander in reversiblen Gleichgewichtszuständen stehenden Teilchen sind durch die kritischen pH-Werte 13 und 9 abgegrenzt. Die Gleichgewichte stellen sich praktisch momentan ein; eine Zeit- oder Temperaturabhängigkeit wurde nicht beobachtet.—Aus *Diffusionsmessungen** konnten die Anionengewichte dieser

* Siehe Teil I: G. JANDER und D. ERTEL, *J. Inorg. Nucl. Chem.* **14**, 71 (1960).

[4] H. REMY, *Lehrbuch Anorg. Chem.* 8. Aufl. Bd. II, 105 (1955).

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Teilchen zu ca. 1000 bzw. ca. 3000 abgeschätzt werden. Die in stark alkalischen Niobatlösungen (pH 10–14) vorliegenden beiden Anionentypen unterscheiden sich nur durch ihre Konstitution, nicht aber durch ihr Gewicht.—Die *präparativ-analytischen Untersuchungen** von Alkaliniobaten bestätigten und ergänzten diese Ergebnisse indem folgende Salztypen dargestellt werden konnten: $Me_8[Nb_6O_{19}\cdot aq]$, $Me_7[HNb_6O_{19}\cdot aq]$ und $(Me_6[Nb_6O_{18}\cdot aq])_n$ (Me = Na bzw. K). Die Formulierung dieser

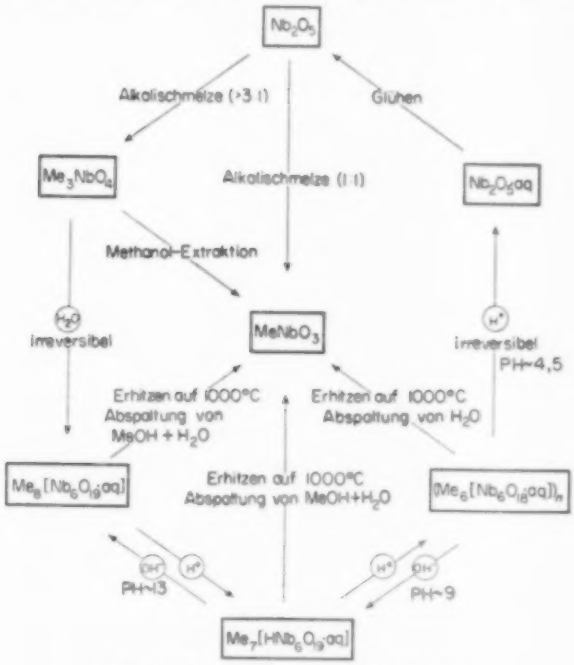

Abb. 5.—Hydrolyseschema der Alkaliniobate.

Verbindungen als Hexaniobate steht im Einklang mit den Ergebnissen der optischen Untersuchungen, ihre Anionengewichte stimmen mit den aus Diffusionsmessungen abgeschätzten gut überein. Durch Erhitzen auf 1000° wandeln sich die Isopolyniobate in Metaniobate $MeNbO_3$ um. Als höchstbasisches Salz konnte aus der NaOH–Nb_2O_5-Schmelze die Verbindung Na_3NbO_4 isoliert werden, die bei Einwirkung von Wasser irreversibel in Hexaniobat, beim Kochen mit absolutem Methanol jedoch solvolytisch in $NaNbO_3$ übergeht.—Aus den Resultaten dieser Untersuchungen ergibt sich folgender in Teilreaktionen gegliederter Hydrolyseverlauf:

$$18MeOH + 3Nb_2O_5 \rightarrow 6Me_3NbO_4 + 9H_2O \qquad \text{(Schmelze)}$$

$$6NbO_4^{3-} + 10H^+ \rightarrow [Nb_6O_{19}\cdot aq]^{8-} + 5H_2O \qquad \text{(irreversibel)}$$

$$[Nb_6O_{19}\cdot aq]^{8-} + H^+ \rightleftharpoons [HNb_6O_{19}\cdot aq]^{7-} \qquad (pH \sim 13)$$

$$[HNb_6O_{19}\cdot aq]^{7-} + H^+ \rightleftharpoons [Nb_6O_{18}\cdot aq]^{6-} + H_2O \qquad (pH \sim 9)$$

$$[Nb_6O_{18}\cdot aq]^{6-} + 6H^+ \rightarrow H_6[Nb_6O_{18}\cdot aq] \qquad (pH \sim 4{\cdot}5)$$

$$\downarrow$$

$$3Nb_2O_5\cdot aq + 3H_2O \qquad \text{(irreversibel)}$$

* Siehe Teil II: G. Jander und D. Ertel, *J. Inorg. Nucl. Chem.* **14**, 77 (1960)

Konduktometrische Titrationen der verschiedenen Salztypen mit verdünnten Mineralsäuren bestätigten diesen Reaktionsmechanismus.—*Vergleichende röntgenographische Untersuchungen* ergaben für jeden Salztyp ein individuelles Debyeogramm. Die thermische Zersetzung der Alkalihexaniobate zu Metaniobaten konnte röntgenographisch nachgewiesen werden.

Die Durchführung dieser Untersuchungen wurde uns durch eine Gewährung von ERP-Mitteln ermöglicht, wofür wir auch an dieser Stelle danken.

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THE KINETICS OF THE REACTION BETWEEN PLUTONIUM(IV) AND VANADIUM(III) IN PERCHLORATE SOLUTION

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Abstract—The kinetics of the reduction of Pu(IV) with V(III) has been studied as a function of temperature and acidity in perchlorate solutions of ionic strength two. The reaction rate has been found to be first order with respect to each of the reactants and inversely proportional both to the first power and to the second power of the hydrogen ion concentration. Thermodynamic quantities for the activation process in terms of the principal species have been obtained for the parallel paths at 25°. It has been shown that the rate of the reduction reaction was unaffected by the presence of added chloride ion, and it appears that the chloride ion does not function as a bridging group in the activated complex. The entropies of the activated complexes for both hydrogen ion dependent paths have been calculated and compared with reactions involving similar charge types.

IN a recent review[1] of the kinetics of oxidation–reduction reactions of uranium, neptunium and plutonium in aqueous acid solution, it was shown that the charge on the activated complex is a factor which is important in the determination of the value of its entropy. In the present work, additional kinetic information has been obtained for reactions in which the principal species carry charges of +3 and +4. Although the results of this work support the general relationship between the charge and the entropy of the activated complex, from the increasing spread of values found for the different charge types, it is clear that there are additional unresolved factors which are operative.

EXPERIMENTAL

Apparatus. Spectrophotometric measurements were made with the Cary Model 14 recording instrument. The thermostated spectrophotometric cell holder and the electrolysis vessel for the preparation of vanadium(III) perchlorate have been described previously.[2] A maximum chart speed of 8 in. per minute was found to be adequate to follow the course of the reaction at a temperature of 20° in 0·25 M perchloric acid. A ruled transparent template was placed over the chart recording to permit optical densities to be read at 1 sec intervals for the more rapid reactions. A double chambered 10 cm spectrophotometric cell was flushed with nitrogen and the reactant solutions were placed in the separate legs. After attaining temperature equilibrium in a water thermostat, the solutions were rapidly mixed and placed in the cell compartment of the spectrophotometer. First readings were obtained within 15 sec after mixing.

Analyses. The initial concentration of Pu(IV) was computed from the known weight of 1/10 N potassium dichromate solution used to oxidise a weighed aliquot of Pu(III). Molar absorptivities of Pu(III) and Pu(IV) were measured in each experiment under the conditions of the kinetic study. Only partial oxidation of the Pu(III) was attempted to avoid the possibility of the formation of Pu(V) or Pu(VI). The Pu(IV) concentration at a given time during the kinetic experiment was computed from the measured optical density at 4695 Å with corrections applied for the contributions of Pu(III), Cr(III), V(III) and VOH^{2+}. A value of 2×10^{-3} for the hydrolysis constant of V(III) together with a

[1] T. W. NEWTON and S. W. RABIDEAU, *J. Phys. Chem.* **63**, 365 (1959).
[2] S. W. RABIDEAU, *J. Phys. Chem.* **62**, 414 (1958).

molar absorptivity of 130 M^{-1} cm^{-1} were used to make the minor correction to the optical density for the presence of VOH^{2+}.[3] The concentration of vanadium(III) perchlorate was determined at 3960 Å with the thiocyanate–acetone method of analysis.[4] A platinized platinum wire was placed in the vanadium(III) perchlorate stock solution to catalyse the oxidation by hydrogen ion of small amounts of V(II) formed in the electrolytic reduction of V_2O_5. Analyses were made for chloride ion in the V(III) stock at the termination of electrolysis with negative results. Only very small amounts of chloride were formed over a period of a week in the V(III) stock kept at 0°. Because V(III) is slowly oxidized by oxygen at a rate inversely proportional to the hydrogen ion concentration and directly proportional to the partial pressure of the oxygen,[5] the V(III) stock solutions were prepared in molar perchloric acid and the storage flasks were flushed with helium and stored at 0°. To measure the rate of change of the concentration of the V(III) stock, samples of the V(III) were quenched in a given volume of standard ceric sulphate. The change in the Ce(IV) concentration was determined spectrophotometrically. Over a period of 3 hr at room temperature, no perceptible change in the V(III) concentration was found. Over a three day period at 0°, the stock changed its titre only a few per cent.

Materials. Baker analysed grade 71 per cent perchloric acid was boiled to eliminate traces of organic material and then flushed with helium over a period of several hours to remove traces of chlorine and chlorine oxides. A weight aliquot of the boiled 71 per cent perchloric acid was standardized against Baker analysed grade mercuric oxide. Sodium perchlorate was prepared from Merck reagent grade sodium carbonate and perchloric acid. The salt was recrystallized from water and dried at 120°. Mallinckrodt reagent grade ammonium thiocyanate was recrystallized from absolute methanol and dried with a stream of air as suggested by CROUTHAMEL and JOHNSON[6] for the use of this reagent in the thiocyanate–acetone method of analysis for vanadium. Vanadium standard solutions were prepared by the dissolution of fused 99·7 per cent pure vanadium metal obtained from A. D. McKay Co. in a hydrochloric–nitric acid mixture. The solution was evaporated to dryness repeatedly, and concentrated hydrochloric acid was used to dissolve the residue. Plutonium(III) solutions were prepared from high purity metal by the addition of a known weight to an appropriate weighed quantity of standardized 71 per cent perchloric acid. Plutonium(III) was oxidized to Pu(IV) with a weighed quantity of 1/10 N potassium dichromate solution prepared from the U.S. National Bureau of Standards sample 136a. All distilled water was redistilled from alkaline permanganate in an all-Pyrex glass still, and conductivity checks were made frequently to monitor the purity of the water. Reported solution concentrations correspond to a temperature of 23°, no correction was applied for temperature changes between 2·4 and 20°.

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RESULTS

By analogy with the results obtained in the kinetic study of the reaction between Pu(VI) and V(III),[7] it was predicted at the onset of this research that on the basis of charge and on the relative ease of formation of the first hydrolysed species of Pu(IV) as compared to Pu(VI), the reaction between Pu(IV) and V(III) would also involve parallel paths dependent upon both the inverse first and the inverse second powers of the hydrogen ion concentration. This prediction has been borne out by the experimental results.

Reaction order and stoicheiometry. To perform stoicheiometry checks, less than an equimolar quantity of V(III) stock was added to a solution of plutonium(IV) perchlorate in 2 M perchloric acid at 2·4°. The concentration of the V(III) stock had been determined by the thiocyanate–acetone method. The formation of Pu(III) as the reduction product was evident from the disappearance of the Pu(IV) peak at 4695 Å, and the formation of the characteristic blue colour of Pu(III). This was confirmed by noting the Pu(III) peaks at 5600 and 6000 Å. After the reaction had

[3] S. C. FURMAN and C. S. GARNER, *J. Amer. Chem. Soc.* **72**, 1785 (1950).
[4] C. E. CROUTHAMEL, B. E. HJELTE and C. E. JOHNSON, *Analyt. Chem.* **27**, 507 (1955).
[5] J. B. RAMSEY, R. SUGIMOTO and H. DE VORKIN, *J. Amer. Chem. Soc.* **63**, 3480 (1941).
[6] C. E. CROUTHAMEL and C. E. JOHNSON, *Analyt. Chem.* **26**, 1284 (1954).
[7] S. W. RABIDEAU, *J. Phys. Chem.* **62**, 414 (1958).

progressed to completion as evidenced by no change in the optical density of the solution at 4695 Å over a period of about 10 min, the change in the Pu(IV) concentration was computed. The difference in the Pu(IV) concentration corresponded to a one-electron change in the V(III). Thus, the reaction stoicheiometry is given by the equation

$$Pu^{4+} + V^{3+} + H_2O = Pu^{3+} + 2H^+ + VO^{2+} \quad (1)$$

The reaction between Pu(IV) and V(III) has been shown to be second order from the usual graphical plot. The linearity of these second order plots was found to extend to 90–95 per cent of completion both for the condition in which the reactants were initially present in equimolar amounts and for the case in which a twofold excess of one of the reactants was used.

Hydrogen ion concentration dependence. Measurements of the rate of reaction between Pu(IV) and V(III) were made in solutions of ionic strength two over an acidity range between 0·25 and 2·00 M at 2·4°. It was not feasible at this temperature to make measurements at acidities much below 0·25 M because of the very rapid reaction rate under these conditions. In addition to the rate measurements at 2·4°, studies were also made of the hydrogen ion concentration dependence of the reaction rate at 6·2, 10·2, 15·4 and 20·0°. The ionic strength was maintained at two with the addition of sodium perchlorate. Upon analysis of the kinetic results, it was concluded that both an inverse first and an inverse second power of the hydrogen ion concentration were involved in the rate law. If the rate law is written in terms of the principal species,

$$-d[\text{Pu(IV)}]/dt = k_1[Pu^{4+}][V^{3+}][H^+]^{-1} + k_2[Pu^{4+}][V^{3+}][H^+]^{-2} \quad (2)$$

With the association quotient for the hydrolysis of Pu(IV) defined by the relation

$$K = [PuOH^{3+}][H^+]/[Pu^{4+}] \quad (3)$$

it is possible to show that the relationship between the unhydrolysed and the total tetravalent plutonium is

$$[Pu^{4+}] = [\text{Pu(IV)}][H^+]/([H^+] + K) \quad (4)$$

where Roman numerals are used to represent total concentrations. With the substitution of equation (4) into equation (2), it follows that

$$-d[\text{Pu(IV)}]/dt = k_1[\text{Pu(IV)}][V^{3+}]/([H^+) + K) + k_2[\text{Pu(IV)}][V^{3+}]/[H^+]([H^+] + K) \quad (5)$$

With the substitution of k_0, the experimentally observed rate constant, for the specific rate constants for the two paths in equation (5), where

$$k_0 = k_1/([H^+] + K) + k_2/[H^+]([H^+] + K) \quad (6)$$

then,

$$-d[\text{Pu(IV)}]/dt = k_0[\text{Pu(IV)}][V^{3+}] \quad (7)$$

Values of the Pu(IV) hydrolysis quotient in perchlorate solutions of ionic strength two were taken from previously published work.[8] The equilibrium quotients for the Pu(IV) hydrolysis at temperatures between 2·4 and 10·2° were calculated with values of 7·3 kcal/mole for ΔH and 19 e.u. for ΔS.

[8] S. W. Rabideau, *J. Amer. Chem. Soc.* **79**, 3675 (1957).

The values of the specific rate constants k_1 and k_2 in equation (6) were obtained from plots of $k_0([H^+] + K)$ vs. $1/[H^+]$. The intercepts and the slopes of these plots are equal to the values of k_1 and k_2, respectively. At 2·4°, the specific rate constants are $k_1 = 1{\cdot}70 \pm 0{\cdot}02$ sec^{-1} and $k_2 = 1{\cdot}71 \pm 0{\cdot}06$ M sec^{-1}, where the uncertainties given correspond to the standard deviations. In Table 1, a comparison is given between the experimentally observed values of k_0 as defined by equation (7) and the calculated values of k_0 obtained by the insertion of the above values of k_1 and k_2 into equation (6).

TABLE 1.—HYDROGEN ION CONCENTRATION DEPENDENCE OF REACTION BETWEEN Pu(IV) AND V(III) IN PERCHLORATE SOLUTION OF IONIC STRENGTH TWO AT 2·4°

[Pu(IV)] (M)	[V(III)] (M)	[H$^+$] (M)	k_0(exptl) (M^{-1} sec^{-1})	k_0(calc) (M^{-1} sec^{-1})
$1{\cdot}334 \times 10^{-3}$	$1{\cdot}168 \times 10^{-3}$	2·000	1·25	1·26
1·665	2·304		1·30	
2·516	1·244		1·30	
1·350	1·665		1·28	
2·145	1·455		1·28	
2·338	1·692	1·000	3·62	3·35
1·762	3·293		3·84	
1·378	1·632		3·38	
1·514	1·570		3·30	
1·850	1·488		3·35	
1·636	1·480		3·19	
1·328	1·802	0·500	9·38	9·87
2·865	1·769		9·38	
1·434	1·532		8·76	
2·052	1·632		9·26	
2·667	1·502		9·10	
1·566	1·607	0·250	30·10	31·75
1·561	1·622		29·83	
1·792	1·501		33·73	
1·772	1·491		32·96	
2·033	1·477		29·94	
1·235	1·510		30·12	

Whereas in molar perchloric acid the two paths contribute very nearly equally to the observed rate at 2·4°, in 0·25 M perchloric acid the k_2 path makes a fourfold greater contribution.

Temperature dependence. The temperature coefficients of the values of k_1 and k_2 were derived from measurements of k_0 as functions of acidity between 2·4 and 20°. In Fig. 1 plots of log k_1 vs. $1/T$ and log k_2 vs. $1/T$ are given. From the slopes of these straight lines, activation energies of $17{\cdot}7 \pm 0{\cdot}5$ kcal/mole and $22{\cdot}1 \pm 0{\cdot}41$ kcal/mole were found for the k_1 and the k_2 paths, respectively. The data are summarized in Table 2. From expressions of the transition state theory,[9] values of the thermodynamic

[9] S. GLASSTONE, K. LAIDLER and H. EYRING, *The Theory of Rate Processes* p. 417. McGraw-Hill, New York (1941).

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quantities of activation for the two paths were computed and are given in Table 3. The method of least squares was applied in obtaining the activation energies and the uncertainties are equal to the standard deviations. An extrapolation of the straight

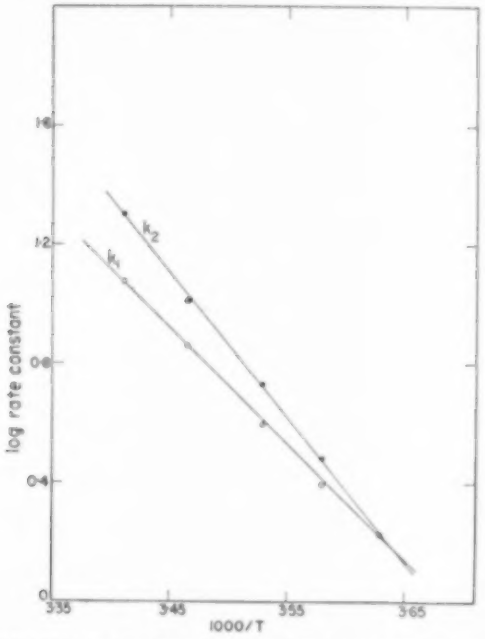

FIG. 1.—Arrhenius plots for the inverse first and the inverse second powered hydrogen ion concentration dependent paths in the reaction between Pu(IV) and V(III).

TABLE 2.—TEMPERATURE DEPENDENCE OF SPECIFIC RATE CONSTANTS FOR THE REACTION BETWEEN Pu(IV) AND V(III) IN PERCHLORATE SOLUTIONS OF $\mu = 2$

Temperature (°C)	k_1 (sec^{-1})	k_2 ($M\ sec^{-1}$)
2·4	1·70	1·71
6·2	2·50	3·04
10·2	3·95	5·39
15·4	7·25	10·7
20·0	11·9	20·1

line relations between $\log k_1$ vs. $1/T$ and $\log k_2$ vs. $1/T$ was made using the least square values of the slope to obtain k_1 and k_2, and hence the associated thermodynamic quantities at a temperature of 25°.

Chloride ion dependence. Although no detectable chloride ion was found in the vanadium(III) perchlorate stock solution at the termination of electrolysis, perchlorate ion is slowly reduced to chloride ion by V(III). To determine whether the chloride ion

could serve as a bridge in the activated complex, rate measurements were made in 0·25 M perchloric acid at 2·4° with a chloride ion concentration of 0·225 M. The ionic strength was maintained at two with the addition of sodium perchlorate. Within experimental error, the value of k_0 was unchanged by the substitution of chloride ion for perchlorate. Thus, it appears that the failure of chloride ion to serve as a bridging

TABLE 3.—THERMODYNAMIC QUANTITIES OF ACTIVATION FOR THE REACTION BETWEEN Pu(IV) AND V(III) AT 25°

	ΔF^* (kcal/mole)	ΔH^* (kcal/mole)	ΔS^* (e.u.)
k_1 path	15·68 ± 0·01	17·1 ± 0·5	4·76 ± 1·7
k_2 path	15·30 ± 0·01	21·5 ± 0·4	20·8 ± 1·4

group in the activated complex arises from the requirement of an oxygen for the formation of the VO^{2+} ion.

Comparison of entropies of activated complexes. The entropies for a number of activated complexes have been computed from the ΔS^* for the reaction and the standard entropies of the reactants written in terms of the principal species.[1] The entropies of activated complexes have been computed with the convention that $S^0_{H^+} = 0$ and with the entropy values for the plutonium ions as given by KATZ and SEABORG[10], and with the values of −63 and −65 e.u. for Ti^{3+} and V^{3+}, respectively, based upon

TABLE 4.—THERMODYNAMIC QUANTITIES OF ACTIVATION FOR REACTIONS OF PLUTONIUM WITH Ti(III) AND V(III) IN PERCHLORATE SOLUTION AT 25°

	ΔH^* (kcal/mole)	ΔS^* (e.u.)	$S^*_{complex}$ (e.u.)	Ref.
(1) $Pu^{4+} + Ti^{3+} + H_2O = (*)^{6+} + H^+$	16·7	5·9	−125	11
(2) $Pu^{4+} + V^{3+} + H_2O = (*)^{6+} + H^+$	17·1	4·76	−128	(this work)
(3) $Pu^{4+} + V^{3+} + H_2O = (*)^{5+} + 2H^+$	21·5	20·8	−112	(this work)
(4) $PuO_2^{2+} + Ti^{3+} + H_2O = (*)^{4+} + H^+$	10·3	−14·7	−92	12
(5) $PuO_2^{2+} + V^{3+} + H_2O = (*)^{4+} + H^+$	15·5	−6·1	−81	2

estimates using the charge and radius of the ions. Table 4 lists the thermodynamic quantities of activation for reactions of Pu^{4+} and PuO_2^{2+} with Ti^{3+} and V^{3+}. The $S_{complex}$ values for reactions (1) and (2) of Table 4 are similar; whereas for the corresponding set of reactions (4) and (5), the agreement is not nearly so good. The range of entropy values for the activated complexes of a given charge type[1] has also increased. Apparently, although the charge on the activated complex to a first approximation determines its entropy, there appear to be other factors such as perhaps differences in charge distribution and in numbers of co-ordinated water molecules

[10] J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements* p. 430. Methuen, London (1957).
[11] S. W. RABIDEAU and R. J. KLINE, *J. Phys. Chem.* **64**, In press (1960).
[12] S. W. RABIDEAU and R. J. KLINE, *J. Phys. Chem.* **63**, 1502 (1959).

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involved in the reaction which have not been taken into consideration. In the reaction of Pu(IV) with V(III), although the path involving the inverse second power of the hydrogen ion concentration has a heat of activation 4·4 kcal/mole greater than the inverse first power path, the greater disorder in the activated complex compensates for the higher heat and both paths contribute significantly to the observed reaction rate. In fact, in solutions of low acidity, the inverse second powered hydrogen ion concentration path makes the major contribution. This does not appear to be the case for the reaction between Pu(IV) and Ti(III) however, since a path in which an inverse second power of the hydrogen ion concentration is involved is not observed.

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HOMOGENER UND HETEROGENER ISOTOPENAUSTAUSCH Fe^{II}/Fe^{III}

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Abstract—The homogeneous isotopic exchange in aqueous solution is strongly catalysed by sulphuric acid. Sulphuric acid exists predominantly in the form of HSO_4^- ions and therefore is able to effect the transfer of hydrogen atoms along hydrogen bonds.

The heterogeneous isotopic exchange between Fe^{II} ions in solution and the solid water-free sulphate of Fe^{III} is also effected by the mutual change of the oxidation state. The rate determining step is preceded by a dissociation equilibrium of the hydrated Fe^{II} ions; in that equilibrium hydrogen atoms are probably formed, which transfer a negative charge to the Fe^{III} ions of the solid sulphate.

1. EINLEITUNG

Zu den Isotopenaustauschreaktionen werden auch Oxydations-Reduktionsreaktionen vom Typus

$$Fe^{II}(\text{gelöst}) + {}^*Fe^{III}(\text{gelöst}) \rightleftharpoons Fe^{III}(\text{gelöst}) + {}^*Fe^{II}(\text{gelöst}) \qquad (1)$$

gerechnet; diese Oxydations-Reduktionsreaktionen werden häufig als Elektronenaustauschreaktionen bezeichnet,[1–5] da die wechselseitige Änderung der Oxydationsstufe formal durch einen Elektronenübergang beschrieben werden kann.

Die Kinetik derartiger Reaktionen kann mit Hilfe radioaktiver Indikatoren untersucht werden. Dabei ist wichtig, dass während der Trennung der Komponenten kein Austausch stattfindet.

Eine geeignete Trennungsmethode für Fe^{II}/Fe^{III} wurde von DODSON[1] gefunden und auch von anderen Autoren benutzt.

DODSON stellte fest, dass der homogene Isotopenaustausch Fe^{II}/Fe^{III} (Gl. 1) in wässrigen Lösungen eine Reaktion 2. Ordnung ist und mit messbarer Geschwindigkeit abläuft. Die Isotopenaustauschgeschwindigkeit ist bei höheren p_H-Werten—d.h. mit fortschreitender Hydrolyse—grösser; sie steigt ausserdem mit wachsender Chloridionenkonzentration gleichmässig an. (Aus den Messungen von SILVERMAN und DODSON[2] bei 20°C und der Ionenstärke 0·55 erhält man für die Geschwindigkeitskonstante etwa $k = 3{\cdot}1\left(1 + \frac{1{\cdot}1}{[H^+]}\right)(1 + 5{\cdot}3[Cl^-])$ 1 Mol^{-1} sec^{-1}.) Der Einfluss von Fluoridionen und von Rhodanidionen auf den homogenen Isotopenaustausch Fe^{II}/Fe^{III} wurde von HUDIS und WAHL[6] und von LAURENCE[4,5] untersucht. Sowohl Fluoridionen als auch Rhodanidionen bilden—ähnlich wie Chloridionen—mit

[1] R. W. DODSON, *J. Amer. Chem. Soc.* **72**, 3315 (1950).
[2] J. SILVERMAN u. R. W. DODSON, *J. Phys. Chem.* **56**, 846 (1952).
[3] J. HUDIS u. R. W. DODSON, *J. Amer. Chem. Soc.* **78**, 911 (1956).
[4] G. S. LAURENCE, *Trans. Faraday Soc.* **53**, 1326 (1957).
[5] F. S. DAINTON, G. S. LAURENCE, W. SCHNEIDER, D. R. STRANKS u. M. S. VAIDYA in R. C. EXTERMANN, *Radioisotopes in Scientific Research* Vol. 2, S. 305. Pergamon Press, London (1958).
[6] J. HUDIS u. A. C. WAHL, *J. Amer. Chem. Soc.* **75**, 4153 (1953).

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Eisenionen Komplexverbindungen; diese Komplexbildung hat ebenfalls nur einen verhältnismässig geringen Einfluss auf die Geschwindigkeit des Isotopenaustausches. Mit Eisen(III)-azidionen wurden ähnlich hohe Austauschgeschwindigkeiten beobachtet wie bei höheren p_H-Werten.[5] Alle diese Untersuchungen wurden in Perchlorsäure-haltigen Lösungen ausgeführt.

Als Reaktionsmechanismus für den homogenen Isotopenaustausch wurde eine Übertragung von Wasserstoffatomen über Wasserstoffbrückenbindungen vorgeschlagen[7] nach dem Schema

$$(H_2O)_5\overset{II}{Fe}{}^{++}\underset{H}{OH}\cdots\underset{H}{O}\overset{III}{Fe}{}^{++}(H_2O)_5 \rightleftharpoons (H_2O)_5\overset{III}{Fe}{}^{++}\underset{H}{O}\cdots\underset{H}{HO}\overset{II}{Fe}{}^{++}(H_2O)_5 \qquad (2)$$

In guter Übereinstimmung mit diesem Reaktionsmechanismus wurde in D_2O eine um den Faktor 2 geringere Geschwindigkeit für den Isotopenaustausch gefunden als in H_2O.[3]

Im Gegensatz zu den Untersuchungen in wässrigen Lösungen verlief der Isotopenaustausch zwischen Ferrocen [Bis(cyclopentadienyl)-eisen(II)] und Ferrociniumsalz [Bis(cyclopentadienyl)-eisen(III)-nitrat oder-perchlorat] in alkoholischer Lösung unmessbar rasch.[5] Hier liegen keine Ionen gleicher Ladung vor, die sich gegenseitig abstossen, sondern ungeladene Moleküle; ein direkter Elektronenübergang zwischen den Chelatkomplexen des Fe^{II} und des Fe^{III} ist denkbar.

2. EXPERIMENTELLER TEIL

Die von DODSON[1] benutzte Trennungsmethode für Fe^{II} und Fe^{III} hat gewisse Nachteile: Das Tris($\alpha\alpha'$-dipyridyl)-eisen(II)-salz haftet in merklichem Umfang am festen Eisenhydroxyd. Darauf haben bereits HUDIS und WAHL[6] hingewiesen. Ausserdem können kleine Mengen Fe^{III} nur nach Zugabe eines Trägers abgetrennt werden. Um die dadurch bedingten Fehlerquellen zu vermeiden und auch kleine Mengen Fe^{III} ohne Zugabe eines Trägers abtrennen zu können, wurde ein anderes Trennungsverfahren ausgearbeitet:[8] Entlüftete Lösungen von Ammoniumacetat ($p_H = 6$), $\alpha\alpha'$-Dipyridyl Kohlenstofftetrachlorid und Acetylaceton wurden in einem Scheidetrichter vorgelegt. Nach Zugabe der Probe wurde sofort extrahiert. Fe^{II} und Fe^{III} wurden in den beiden getrennten Phasen direkt kolorimetrisch bestimmt.

Die Untersuchung des homogenen und des heterogenen Isotopenaustausches wurde in der gleichen Apparatur vorgenommen. Diese machte es möglich, während des Versuches laufend Proben zu entnehmen. Eine Glasfritte verhinderte das Eindringen von Kristallen bei der Probenahme während des heterogenen Isotopenaustausches.

Die Eisen(II)-bzw. Eisen(III)-salz-Lösungen waren mit ^{59}Fe höherer spezifischer Aktivität (10 C/g) markiert, das aus Amersham (England) bezogen wurde. Die Aktivität wurde in einem Flüssigkeitszählrohr gemessen, und zwar die Aktivität des Fe^{II} in der wässrigen Phase, die Aktivität des Fe^{III} in der Kohlenstofftetrachloridphase.

3. HOMOGENER ISOTOPENAUSTAUSCH

Die Ergebnisse einer Messung des homogenen Isotopenaustausches Fe^{II}/Fe^{III} in Perchlorsäure sind in Abb. 1 wiedergegeben. Die Vorteile der Trennungsmethode machten sich dabei besonders bemerkbar. Die Ergebnisse der Messungen des homogenen Isotopenaustausches Fe^{II}/Fe^{III} in Perchlorsäure stehen in guter Übereinstimmung mit den Ergebnissen anderer Autoren.[2]

Für die Geschwindigkeitskonstante k des homogenen Isotopenaustausches bei

[7] R. W. DODSON, *J. Phys. Chem.* **56**, 852 (1952); R. W. DODSON u. N. DAVIDSON, *Ibid.* **56**, 866 (1952).
[8] K. H. LIESER u. H. SCHROEDER, *Z. Anal. Chem.* im Drück.

20°C in 0·5 m-Perchlorsäure und in Gegenwart von 10^{-2} Mol/Liter Kaliumrhodanid folgt z.B. $k = 12{\cdot}3$ l. Mol^{-1} sec^{-1}. Geschwindigkeitskonstante k und Halbwertzeit $t_{1/2}$ für den Austausch sind durch die Beziehung

$$k = \frac{\ln 2}{t_{1/2}([Fe^{II}] + [Fe^{III}])} \tag{3}$$

miteinander verknüpft.

Überraschenderweise wurde bei Verwendung von Schwefelsäure anstelle von Perchlorsäure eine ausserordentlich hohe Geschwindigkeit für den homogenen

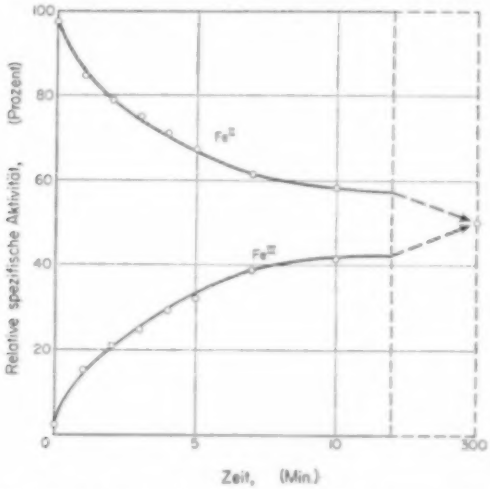

ABB. 1.—Die Änderung der spezifischen Aktivität beim homogenen Isotopenaustausch zwischen Fe^{II} (10^{-4} Mol/Liter, mit ^{59}Fe markiert) und Fe^{III} (10^{-4} Mol/Liter) in 0·5 molarer Perchlorsäure.

Isotopenaustausch Fe^{II}/Fe^{III} beobachtet. Die Austauschreaktion war bei einer Konzentration von je 10^{-4} Mol/Liter Fe^{II} und Fe^{III} in 1-molarer Schwefelsäure bereits nach 1 Minute beendet. In Gegenwart von Rhodanidionen ergab sich dasselbe Bild.

Legt man für den Isotopenaustausch in 1-molarer Schwefelsäure ebenfalls eine Reaktion 2. Ordnung zugrunde, so berechnet man unter Berücksichtigung der Messfehler, dass die Geschwindigkeitskonstante k der Isotopenaustauschreaktion in 1-molarer Schwefelsäure grösser ist als 320 l. Mol^{-1} sec^{-1}. D.h. der homogene Isotopenaustausch Fe^{II}/Fe^{III} verläuft unter sonst gleichen Bedingungen in 1-molarer Schwefelsäure um mehr als den Faktor 26 schneller als in 0·5-molarer Perchlorsäure. Dies kann nicht auf dem Einfluss der Wasserstoffionenkonzentration beruhen (vgl. Abschnitt 1), sondern nur auf der Anwesenheit der Sulfationen. Damit kommt man zu dem Ergebnis, dass die Isotopenaustauschgeschwindigkeit durch Sulfationen mindestens 10 mal so stark erhöht wird wie durch Chloridionen, Fluoridionen oder Rhodanidionen der gleichen Molarität.

Schwefelsäure liegt in 1-molarer Lösung zu etwa 85 Prozent in Form von HSO_4^--Ionen vor.[9] Diese Ionen vermögen sich infolge ihrer negativen Ladung bevorzugt

[9] H. S. HARNED u. B. B. OWEN, *Physical Chemistry of Electrolytic Solutions* S. 610. Reinhold, New York (1950).

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an die positiv geladenen Eisenionen anzulagern, wodurch eine Übertragung von Wasserstoffatomen über Wasserstoffbrückenbindungen möglich wird, etwa nach dem Schema

$$(H_2O)_5\overset{II}{Fe}{}^{+}\overset{O}{\underset{O}{OSOH}}\cdots\overset{III}{\underset{H}{OFe}}{}^{2+}(H_2O)_5 \rightleftharpoons (H_2O)_5\overset{III}{Fe}{}^{+}\overset{O}{\underset{O}{OSO}}\cdots\overset{II}{\underset{H}{HOFe}}{}^{2+}(H_2O)_5 \quad (4)$$

oder

$$(H_2O)_5\overset{II}{Fe}{}^{+}\overset{O}{\underset{O}{OSOH}}\cdots\overset{O}{\underset{O}{OSOFe}}{}^{+}\overset{III}{(H_2O)_5} \quad (H_2O)_5\overset{III}{Fe}{}^{+}\overset{O}{\underset{O}{OSO}}\cdots\overset{O}{\underset{O}{HOSOFe}}{}^{+}\overset{II}{(H_2O)_5} \quad (5)$$

Der Mechanismus des homogenen Isotopenaustausches ist dann in Gegenwart von Schwefelsäure der gleiche wie in Abwesenheit von Schwefelsäure (Gl. (2)); er

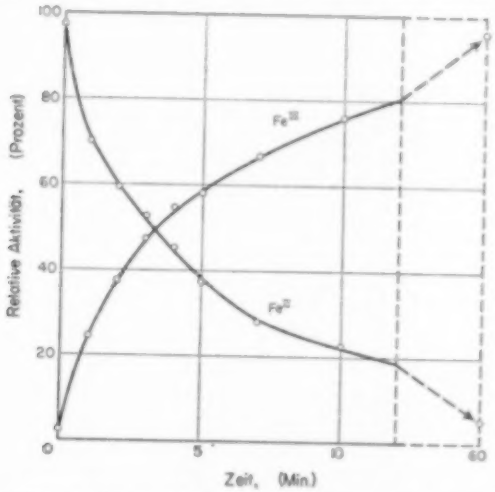

Abb. 2.—Aktivitätsverlauf in der Lösung beim heterogenen Isotopenaustausch zwischen Fe^{II} (gelöst, 10^{-4} Mol/Liter, mit ^{59}Fe markiert) und Fe^{III} des wasserfreien Eisen(III)-sulfats während der Auflösung des wasserfreien Eisen(III)-sulfats in 0.5 molarer Perchlorsäure.

besteht in beiden Fällen in einer Übertragung von Wasserstoffatomen über Wasserstoffbrückenbindungen. Der Isotopenaustausch wird durch Schwefelsäure in ähnlicher Weise katalysiert wie beispielsweise durch die Hydroxokomplexe des Eisens, die sich bei höheren p_H-Werten bilden.

4. HETEROGENER ISOTOPENAUSTAUSCH

Die Auflösungsgeschwindigkeit des festen wasserfreien Eisen(III)-sulfats in wässrigen Lösungen wird durch die Anwesenheit von Eisen(II)-ionen oder anderen Reduktionsmitteln in der Lösung wesentlich erhöht. Aus diesem Grunde wurde der heterogene Isotopenaustausch Fe^{II}/Fe^{III} zwischen markierten Eisen(II)-ionen in der Lösung und festem wasserfreien Eisen(III)-sulfat untersucht. In Abb. 2 sind die relativen Aktivitäten des Fe^{II} und des Fe^{III} als Funktion der Zeit wiedergegeben. Das Eisen(III)-sulfat geht in Lösung und die Konzentration der Eisen(III)-ionen steigt mit der Zeit an. Gleichzeitig findet in der Lösung der homogene Isotopenaustausch

Fe^{II}/Fe^{III} statt. Infolgedessen steigt die Aktivität des Fe^{III} kontinuierlich an und die Aktivität des Fe^{II} nimmt kontinuierlich ab.

Viel interessanter ist die Aufzeichnung der relativen *spezifischen* Aktivität als Funktion der Zeit (Abb. 3): Kurz nach Beginn des Auflösungsvorgangs besitzt das in der Lösung auftretende Fe^{III} die gleiche spezifische Aktivität wie das vorgelegte Fe^{II}. Im weiteren Verlauf des Auflösungsvorgangs ist die spezifische Aktivität des Fe^{III} höher als die des Fe^{II}; infolge des homogenen Isotopenaustausches Fe^{II}/Fe^{III} in der Lösung nähern sich die spezifischen Aktivitäten allmählich einander und

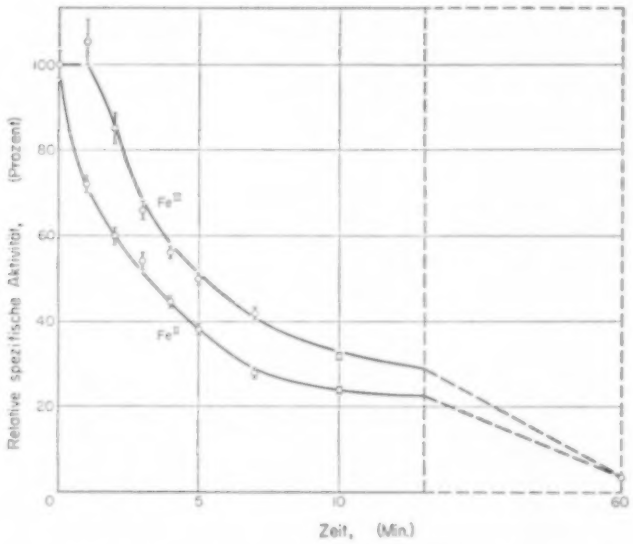

ABB. 3.—Die spezifischen Aktivitäten des Fe^{II} und des Fe^{III} in der Lösung beim heterogenen Isotopenaustausch zwischen Fe^{II}(gelöst) und Fe^{III} des wasserfreien Eisen(III)-sulfats (Versuchsbedingungen wie in Abb. 2 angegeben).

werden schliesslich praktisch gleich. Diese Ergebnisse zeigen, dass bei dem heterogenen Isotopenaustausch das Fe^{III} aus dem vorgelegten markierten Fe^{II} entsteht. Es findet also kein Austausch von Atomen, sondern eine wechselseitige Änderung der Oxydationsstufe—d.h. formal ein Elektronenübergang—statt.

Ein Einfluss der Art der Säure auf die Auflösungsgeschwindigkeit des Eisen(III)-sulfats ist nicht erkennbar. In Schwefelsäure und in Perchlorsäure werden gleiche Auflösungsgeschwindigkeiten gefunden.[10]

Untersucht man die Abhängigkeit der Auflösungsgeschwindigkeit des Eisen(III)-sulfats von der Fe^{II}-Konzentration in der Lösung, so findet man, dass die Auflösungsgeschwindigkeit des Eisen(III)-sulfats mit der Quadratwurzel aus der Fe^{II}-Konzentration ansteigt.[10] Diese Gesetzmässigkeit deutet darauf hin, dass dem Geschwindigkeits-bestimmenden Schritt des Auflösungsvorgangs ein Dissoziationsgleichgewicht der hydratisierten Eisen(II)-ionen vorgelagert ist.

Das Dissoziationsgleichgewicht könnte nach zwei verschiedenen Mechanismen

[10] K. H. LIESER u. H. SCHROEDER, *Z. Elektrochem*, im Druck.

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zustande kommen, die sich formal durch die Gleichungen (6) bzw. (7) beschreiben lassen:

$$Fe^{II}(\text{gelöst}) \rightleftharpoons Fe^{III}(\text{gelöst}) + e^- , \tag{6}$$

$$(H_2O)_5\overset{II}{Fe}{}^{2+}\overset{H}{OH} \rightleftharpoons (H_2O)_5\overset{III}{Fe}{}^{2+}OH + H \tag{7}$$

Im ersten Fall (Gl. 6) sollte die Auflösungsgeschwindigkeit mit steigender Eisen(III)-ionenkonzentration in der Lösung absinken, da die Gleichgewichtskonzentration an Elektronen herabgedrückt würde. Die Auflösungsgeschwindigkeit ist jedoch unabhängig von der Eisen(III)-ionenkonzentration in der Lösung. Obwohl Theorien für den Übergang von Elektronen vorgeschlagen wurden,[11-13] konnte ein direkter Elektronenübergang zwischen gleichgeladenen Ionen in wässrigen Lösungen bisher experimentell noch nicht festgestellt werden.

Sehr viel wahrscheinlicher ist ein Dissoziationsgleichgewicht nach Gl. (7). Ist ein solches Dissoziationsgleichgewicht vorgelagert, so besteht der Mechanismus des heterogenen Isotopenaustausches ebenso wie der Mechanismus des homogenen Isotopenaustausches in der Übertragung einer negativen Ladung durch ein Wasserstoffatom. Beim homogenen Isotopenaustausch hat man Wasserstoffbrückenbindungen anzunehmen; man findet eine Reaktion 2. Ordnung. Beim heterogenen Isotopenaustausch können sich wahrscheinlich deshalb keine Wasserstoffbrückenbindungen ausbilden, weil die Eisen(III)-ionen des festen Eisen(III)-sulfats nicht hydratisiert sind; in diesem Falle entstehen in einem Dissoziationsgleichgewicht aus den hydratisierten Eisen(II)-ionen Wasserstoffatome (Gl. (7)). Der Geschwindigkeits-bestimmende Schritt besteht dann in der Übertragung einer negativen Ladung durch die Wasserstoffatome auf die Eisen(III)-ionen des festen Eisen(III)-sulfats, wobei Eisen(II)-ionen entstehen. Die Hydratisierung dieser Eisen(II)-ionen verläuft verhältnismässig rasch.

[11] W. F. Libby, *J. Phys. Chem.* **56**, 863 (1952).
[12] R. J. Marcus, B. J. Zwolinski u. H. Eyring, *J. Phys. Chem.* **58**, 432 (1954).
[13] R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956); **26**, 867 (1957).

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 104 to 113. Pergamon Press Ltd. Printed in Northern Ireland

SOLUTE–SOLVENT INTERACTION IN THE SYSTEM HYDROCHLORIC ACID–WATER–TRI-n-BUTYL PHOSPHATE

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Abstract—Attempts have been made to identify the species formed in a heterogeneous equilibrium between aqueous hydrochloric acid and pure tributyl phosphate. In addition to the conventional distribution and water content determination, physical–chemical measurements of density, viscosity and conductivity of the organic layer were carried out. Two well defined species were found to exist as a result of solute–solvent interactions in the system studied. The first, formed at lower initial aqueous acid concentrations has the composition $[(TBP)_2 \cdot HCl \cdot (H_2O)_4]$; the second, formed at higher acid concentrations, has the general formula $[TBP \cdot HCl \cdot (H_2O)_3]$. The reactions involved have been suggested. The system studied is of interest in connection with the extraction of inorganic chlorides from hydrochloric acid solutions into tributyl phosphate.

THE development of solvent extraction for both analytical and separation purposes has emphasized the interactions involved in the distribution of inorganic species between water and various organic solvents. In these solute–solvent interactions, the complex-forming property of the organic solvent is considered to be an important factor. One of the more useful solvents for investigation of this kind of reaction is tri-n-butyl phosphate, $(C_4H_9O)_3PO$, (TBP), a basic non-electrolyte, which is widely employed as an excellent extractant of inorganic nitrates from aqueous nitric acid solutions. Since the high complexing ability of the TBP molecule is due to the basic oxygen of the phosphoryl group, it seemed of interest to investigate the interactions involved in the distribution of mineral acids other than nitric[1,2] between water and TBP, and to identify the species extracted. The system $HCl–H_2O$–TBP was chosen in the first instance.

Systems involving hydrochloric acid as extraction-promoting agent have been studied in the distribution of actinides and lanthanides,[3] zirconium,[4] alkali chlorides[5,6] and several other metallic chlorides[7,8] between aqueous acid solutions and TBP. Certain data are available on the distribution of hydrochloric acid between water and TBP,[5,7,8,9] and on the hydration of the acid in the organic phase.[5,8,10]

[1] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52,** 39 (1956).
[2] D. G. TUCK, *J. Chem. Soc.* 2783 (1958).
[3] D. F. PEPPARD *et al.*, *J. Phys. Chem.* **57,** 294 (1953); *J. Amer. Chem. Soc.* **75,** 6063 (1953); *J. Amer. Chem. Soc.* **3,** 370 (1957).
[4] A. E. LEVITT and H. FREUND, *J. Amer. Chem. Soc.* **78,** 1545 (1956).
[5] W. H. BALDWIN, C. E. HIGGINS and B. A. SOLDANO, *J. Phys. Chem.* **63,** 118 (1959).
[6] T. V. HEALY and P. E. BROWN, AERE/CR/1970 (1956).
[7] I. J. GAL and A. RUVARAC, *Bull. Inst. "Boris Kidrich"* **8,** 67 (1958).
[8] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **10,** 306 (1959).
[9] D. F. PEPPARD, G. W. MASON and J. L. MAIER, *J. Inorg. Nucl. Chem.* **3,** 215 (1956).
[10] D. G. TUCK and R. M. DIAMOND, *Proc. Chem. Soc.* 236 (1958).

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However, no results have so far been published showing that in the extraction of this acid its distribution between water and pure TBP is not simple, and that the complexing property of the TBP plays a very important rŏle. In addition, our preliminary results on the extractability of a series of metal chlorides have suggested the need for an investigation of the acidic species existing in, or extracted into, TBP, and for a correlation of the nature of this acidic species with the distribution of metal chloride in each case.

In order to characterize the composition of the species extracted, data are presented in this paper on the physical–chemical nature of the TBP phase. Variations in density, viscosity and conductivity are noted. The swelling of the TBP phase is interpreted, together with its acid and water content, as a function of the acid concentration in the initial aqueous phase with which the TBP was equilibrated. Two well-defined hydrated acid species were found to exist in, or to be extracted into, the organic phase, and evidence for their formation is formulated.

EXPERIMENTAL

Reagents

Baker's "Analysed Reagents" grade hydrochloric acid was standardized against standard carbonate-free sodium hydroxide solutions. Calculated amounts were taken for thirteen stock solutions of various concentrations. TBP, obtained from Commercial Solvents Corporation, was purified by treatment with sodium hydroxide followed by distillation.[11] Excess of water was removed by several treatments with magnesium sulphate, and the final product was stored over anhydrous sodium sulphate in a dark bottle.

Equilibrium and volume change measurements

The swelling of the organic phase, due to the solubility of aqueous hydrochloric acid in it, was measured in 10 ml graduated (0·1 ml) centrifuge tubes; these had been thoroughly cleaned in hot sulphuric acid to ensure complete phase separation. 5 ml of the dried TBP were carefully added from a 10 ml microburette to 5 ml of the initial aqueous hydrochloric acid solution. The interface- and air-menisci were immediately noted. The stoppered tubes were then shaken mechanically for 15 min. Excellent phase separation was ensured after 1 min of centrifugation, and the menisci at equilibrium were read to within ±0·025 ml. The average was taken of at least five determinations, which never differed by more than 2 per cent. The room temperature was 20° ± 1·5° C during these measurements.

Acid distribution measurements

The contents of the five tubes from the equilibrium measurements were poured into one 50 ml centrifuge tube and centrifuged. The organic layer was removed using a pipette with a long drawn-out tip. Aliquots, 5 or 10 ml, of both phases were immediately diluted, the organic phase with a 1:3 water–ethanol mixture, and in each case the acid content was determined by standard alkali. All analyses were performed in duplicate or triplicate. The acidity balance for total hydrogen ion concentration in both the aqueous and organic layers after equilibration agreed within 1 per cent with the amount originally introduced.

Density measurements

Pyknometers of approximately 3 ml capacity were used to determine densities of the freshly-equilibrated organic layers, and were placed in a water bath at a temperature of 20° ± 0·1° C. The density of pure water was taken from LANGE's *Handbook of Chemistry*. The density values were used to calculate viscosity values in centipoises.

[11] J. KENNEDY and S. S. GRIMLEY, AERE/CE/R 968 (1952).

Viscosity measurements

The viscosities of the TBP phases were determined by means of an Ostwald type viscometer calibrated with conductivity water. All measurements were carried out in a thermostatic water bath at 20° ± 0·1°C. The viscosity of pure water was taken from *The International Critical Tables*.

Conductivity measurements

Resistance measurements were carried out using an Industrial Instruments Conductivity Bridge Model RC-216-Bl, and a frequency of 1000 cycles. The cell constant was determined from the specific conductance values of potassium chloride taken from *The Handbook of Physics and Chemistry*. Since the solvent conductance is due solely to the hydrated electrolyte dissolved in it, no solvent correction is necessary.

TABLE 1

No. of soln.	Molarity of HCl			Vol. increase of the organic phase (ml)	α	μ	HCl in the organic phase (mmole)	HCl/TBP ratio	H_2O in the organic phase (mmole)	H_2O/TBP ratio
	In the initial aqueous soln.	In the equil. aqueous phase	In the equil. organic phase							
1	2	3	4	5	6	7	8	9	10	11
1	0·121	0·126	0·0031	0·30	0·025	0·028	0·016	0·0009	18·7	1·0
2	0·243	0·250	0·0073	0·30	0·029	0·033	0·04	0·0022	18·3	1·0
3	0·607	0·616	0·027	0·30	0·044	0·049	0·14	0·0077	18·2	1·0
4	1·215	1·208	0·075	0·30	0·062	0·070	0·40	0·022	18·9	1·0
5	2·429	2·333	0·223	0·30	0·096	0·108	1·18	0·065	20·3	1·1
6	3·644	3·330	0·604	0·45	0·182	0·220	3·26	0·18	28·2	1·5
7	4·859	4·338	1·052	0·70	0·243	0·322	5·99	0·33	39·8	2·2
8	6·351	5·565	1·540	0·90	0·279	0·399	9·09	0·50	51·8	2·8
9	7·288	6·285	1·924	1·00	0·307	0·460	11·50	0·63	55·3	3·0
10	8·892	7·584	2·474	1·15	0·326	0·521	15·22	0·83	56·2	3·1
11	9·717	8·254	2·806	1·25	0·341	0·568	17·50	0·96	55·7	3·0
12	11·431	9·528	3·318	1·45	0·349	0·633	21·40	1·18	56·5	3·1
13	12·146	10·178	3·622	1·55	0·356	0·676	23·72	1·30	55·2	3·0

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Water determinations

The water content of the TBP layer was found by means of the Karl Fischer reagent, using the dead-stop end-point method as determined with a Fisher Titrimeter. The reagent was standardized against a known "Fisher Scientific Reagents" solution of water in methanol. In addition, the reagent was checked by titration against TBP equilibrated with water to prove the feasibility of the method in the presence of TBP. Duplicate trials showed that the results were reproducible to within 3 per cent or better.

RESULTS

Distribution of the acid

Table 1 shows the hydrochloric acid content in the initial aqueous solutions, and the molar concentration of the acid in both aqueous and organic equilibrium layers. column (6) shows the calculated concentration distribution coefficients, α, defined as

$$\alpha = \frac{\text{conc. of HCl in the organic layer}}{\text{conc. of HCl in the aqueous layer}}.$$

In column (7) are given the calculated mass distribution coefficients, μ, defined as

$$\mu = \frac{\text{total amount of HCl in the organic layer}}{\text{total amount of HCl in the aqueous layer}}$$

The relation between these two coefficients is given by

$$\mu = \frac{V_0}{V_a} \cdot \alpha$$

where V_0 and V_a represent the volumes of the equilibrium organic and the equilibrium

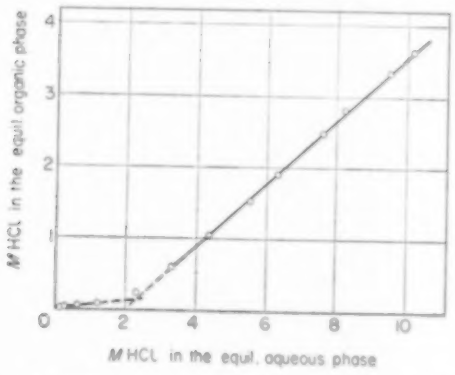

FIG. 1.—HCl molarity in the equilibrium organic phase versus its molarity in the equilibrium aqueous phase.

aqueous layers respectively. The volume increases of the organic phases in ml are given in column (5) of Table 1, and the ratio of the two volumes in column (6) of Table 2. The concentrations of the acid in the equilibrium organic and aqueous phases are plotted in Fig. 1. The distribution isotherm shows that extraction of the HCl from the aqueous into the TBP phase is not uniform: in low-acidity regions the

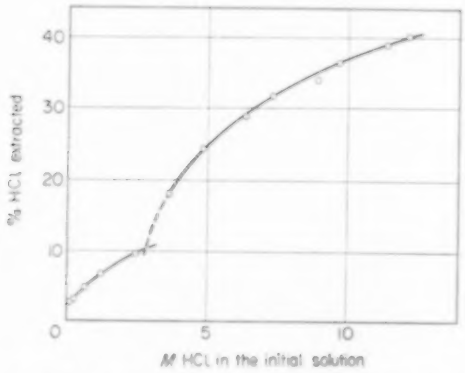

FIG. 2.—Percentage of HCl extracted vs. HCl molarity in the initial aqueous solution.

species extracted differ from those in middle- and high-acidity regions.[9] The break in the curve coincides with the increased swelling of the organic phase and coincides with the break in the curve in Fig. 2, in which the percentage of HCl extracted is plotted against the acid molarity in the initial aqueous solutions.

Swelling of the TBP *phase*

In Fig. 3 the ratio V_0/V_a [Table 2, column (6)] is plotted against the amount in mmoles of hydrochloric acid extracted into TBP. Two breaks are clearly distinguishable. The first corresponds to about 9·1 mmoles of HCl and the second to double

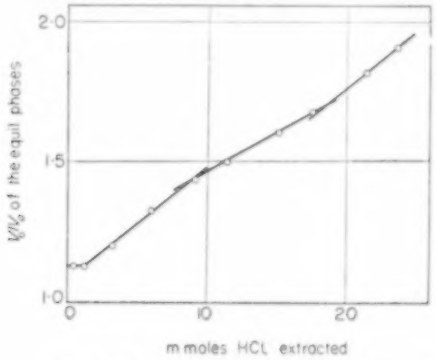

FIG. 3.—The ratio V_0/V_a of phase volumes after equilibration vs. mmoles of HCl extracted.

TABLE 2

No. of soln.	d Density at 20°C (g/cm³)	η Viscosity at 20°C (centipoise)	κ Specific conductance at 20°C (mhos × 10^6)	λ Equivalent conductance at 20°C	Ratio V_0/V_a of the equilibr. phases	α_0 Degree of ionization (%)
1	2	3	4	5	6	7
1	0·978	4·419	0·0029	0·935	1·13	0·07
2	0·978	4·382	0·0068	0·927	1·13	0·07
3	0·979	4·402	0·0184	0·679	1·13	0·05
4	0·982	4·624	0·0499	0·668	1·13	0·05
5	0·985	5·725	0·267	1·203	1·13	0·11
6	0·992	7·106	0·956	1·583	1·20	0·19
7	1·002	10·743	2·088	1·985	1·32	0·36
8	1·011	14·198	2·920	1·970	1·44	0·47
9	1·016	16·928	3·896	2·025	1·50	0·57
10	1·022	20·698	3·855	1·560	1·60	0·54
11	1·028	22·542	3·923	1·398	1·67	0·52
12	1·031	24·465	3·790	1·140	1·82	0·46
13	1·034	25·535	3·366	0·930	1·90	0·40

this amount, 18·25 mmoles. The total amount of tributyl phosphate in 5 ml corresponds to 18·3 mmoles of the ester, neglecting its extremely low solubility (0·04 per cent) in water and aqueous HCl.[12] The two breaks, therefore, correspond to the total formation of the compounds $(TBP)_2 \cdot HCl$ and TBP·HCl respectively. A direct plot of the swelling of the organic phases millilitres in (Table 1, column (5)) against mmoles of HCl extracted, shows the same two breaks at identical TBP : HCl ratios.

[12] C. E. HIGGINS, W. H. BALDWIN and B. A. SOLDANO, *J. Phys. Chem.* **63**, 113 (1959).

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Density of the TBP *phase*

The results of the density measurements carried out on the organic phase in the course of this work are given in column (2) of Table 2. A plot of these values versus the amount of the acid in the organic phase, Fig. 4, gives a curve composed of three parts corresponding to low-, middle- and high-acidity regions. The point at which the first two parts of the curve intersect on extension corresponds to a TBP : HCl ratio of two, corresponding to the formation of $(TBP)_2 \cdot HCl$. The second break, between the second and third parts of the curve, corresponds to a ratio of unity, demonstrating the formation of the compound TBP·HCl.

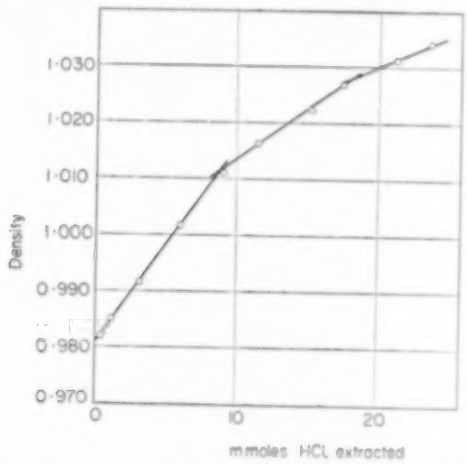

FIG. 4.—Density of the equilibrium organic phase versus mmoles of HCl extracted.

Viscosity of the TBP *phase*

The viscosities in centipoises of the series of solutions of hydrochloric acid in TBP are tabulated in column (3) of Table 2. The curve of viscosity plotted against mmoles of HCl extracted into TBP (Fig. 5) shows only one intersection between the middle- and high-acidity regions, at approximately 18 mmoles of HCl in the organic phase, which can apparently be ascribed to the formation of the compound TBP·HCl. No plausible explanation can be suggested as to why the experimentally determined viscosities do not show evidence for the formation of the first compound.

Conductivity of the TBP *phase*

Data on the specific and equivalent conductances of the organic layers are listed in columns (4) and (5) of Table 2 respectively. Fig. 6 shows the graph of the equivalent conductance λ, plotted against the square root of the acid concentration $\sqrt{c}$, in the organic phase. The beginning of the conductance isotherm is slightly displaced towards low λ values. The curve then rises rather steeply and after a flat maximum, descends steeply as the equivalent conductance decreases. The intersection on extension over the flat maximum corresponds to a TBP : HCl ratio of two, corresponding to the formation of $(TBP)_2 \cdot HCl$.

Water content of the TBP *phase*

Numerical values for the distribution of water into TBP along with the electrolyte are given in columns (10) and (11), Table 1 and in Fig. 7 the extracted H_2O is plotted vs. the extracted HCl in mmoles. The slope of the first part of the curve is equal to

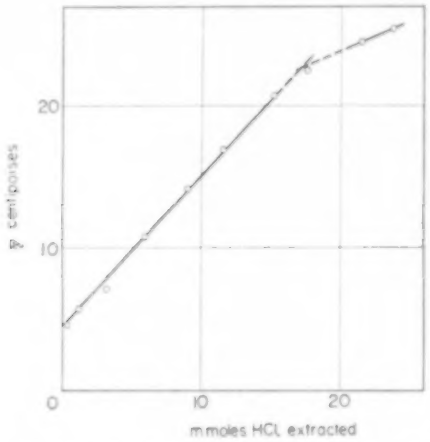

FIG. 5.—Viscosity of the equilibrium organic phase vs. mmoles of HCl extracted.

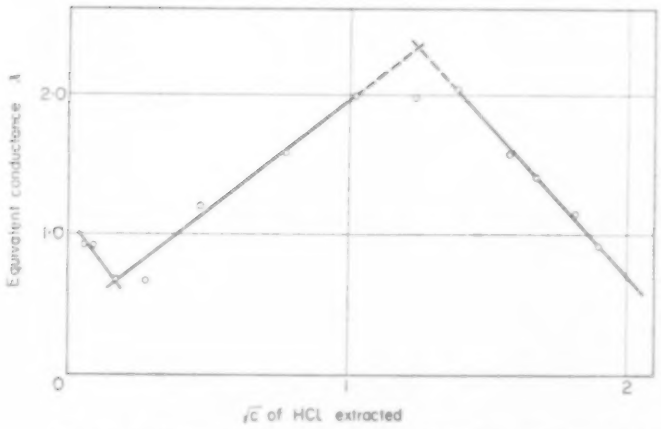

FIG. 6.—Equivalent conductance of the equilibrium organic phase vs. the square root of the HCl concentration in the organic phase.

four, indicating that each hydrochloric acid molecule is accompanied by four water molecules on passing from aqueous solution into TBP. The intersection of the two parts of the curve appears at 9·7 mmoles of HCl, corresponding to a ratio of TBP to HCl of two. From this point onwards the almost horizontal part of the curve indicates that any further hydrochloric acid molecules extracted are no longer hydrated. The amount of water in the organic phase remains essentially constant and equal to a H_2O : HCl ratio of three.

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DISCUSSION

Two well-defined compounds between TBP and hydrochloric acid were detected by the physical–chemical methods used in this research. The ratio TBP : HCl was two in the first compound and unity in the second. The compounds formed between tributyl phosphate and nitric acid,[1,2] and between tributyl phosphate and perchloric acid[15,16] were found to have a TBP : acid ratio of one. Hitherto no TBP-acid compound has been identified with this ratio greater than one. On the other hand,

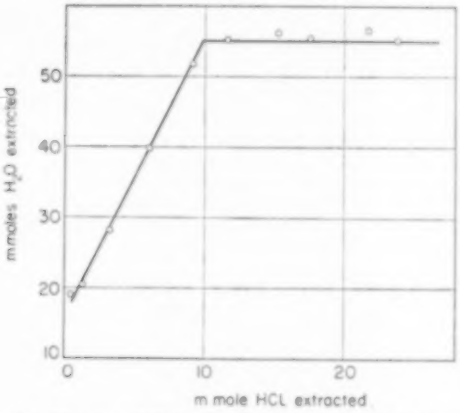

FIG. 7.—Mmoles of H_2O extracted vs. mmoles of HCl, both in the equilibrium organic phases.

nothing can be deduced from the evidence presented in this paper concerning the existence of compounds with a TBP : HCl ratio of less than unity. The existence of such compounds can, however, not be excluded, as a compound containing two molecules of nitric acid to one of TBP has recently been found to be present in systems containing 1 M TBP in benzene as a diluent.[17] This problem is being studied during investigations into the system H_2O–HCl–TBP–diluent, and it is hoped that the results will be published in due course.

An approximate measure of the degree of ionization of the hydrochloric acid in the organic layer was estimated by means of the Walden relation $\lambda\eta/60$. The calculated values, presented in Table 2, column (7), show that hydrochloric acid exists to a large extent in molecular form or as ion-pairs,[18] the degree of ionization, α_0, varying between 0·05–0·57 per cent. When α_0 is plotted against the concentration of the acid in the organic phase, the maximum ionization value corresponds to a TBP : HCl ratio of approximately two.

For some mineral acids, among them hydrochloric acid, a hydration number of four in aqueous solution has been suggested by several authors.[19] Many others have given evidence agreeing with the above result,[5,10,13,20] based on studies of liquid

[13] H. A. C. McKay and A. R. Mathieson, *Trans. Faraday Soc.* **47**, 428 (1951).
[14] D. E. Campbell, H. A. Clark and W. H. Bauer, *J. Phys. Chem.* **62**, 506 (1958).
[15] N. S. Povickii, A. S. Solovkin and I. V. Shilin, *Zh. Neorg. Khim.* **3**, 222 (1958).
[16] V. B. Shevchenko, I. V. Shilin and A. S. Solovkin, *Zh. Neorg. Khim.* **3**, 225 (1958).
[17] V. V. Fromin and E. P. Maierova, *Zh. Neorg. Khim.* **3**, 540 (1958).
[18] R. M. Diamond, *J. Phys. Chem.* **61**, 75 (1957).
[19] K. N. Bascombe and R. P. Bell, *Disc. Faraday Soc.* **24**, 158 (1957).
[20] I. Nelidov and R. M. Diamond, *J. Phys. Chem.* **59**, 710 (1955).

extraction of mineral acids, and have pointed out the significance of the associated water in the extracted species.[21] The large difference in the hydration number of hydrochloric acid when extracted from low and from high aqueous acid concentrations is very probably connected with its proton hydration in the initial aqueous solution. For concentrations of acid up to about 7–8 M in the aqueous solution, the hydration number of four may be taken as correct.[19] At this concentration all the water is combined with the ions, and little exists as free solvent. Therefore, when the concentration of the acid exceeds 8 M, a deficiency of water may be assumed. Thus concentrated hydrochloric acid may act as a dehydrating agent upon a substance possessing loosely-bound water; this dehydrating property of concentrated hydrochloric acid seems to be pronounced in the system under consideration. The first compound identified in this study has a H_2O : HCl ratio of six, but after further extraction of hydrochloric acid, the second compound is formed with a H_2O : HCl ratio of only three. On the other hand, the H_2O : TBP ratio is equal in both the TBP hydrochloric acid compounds identified.

In the hydration of the TBP-mineral acid species in the organic layer, two outstanding differences must be emphasized between the rôle of water in the interaction of nitric acid with TBP and its rôle in the case of hydrochloric acid. The first difference lies in the competition between water and the acid for the available TBP. This competition is characteristic for systems containing nitric acid, but not for those with hydrochloric acid. The formation of the TBP–hydrochloric acid compound passes through the stage of the TBP monohydrate molecule only, and the second difference is concerned with this phenomenon. There seems to exist today a unanimous belief[2,5] that there are no hydrated nitric acid-TBP compounds; our results, on the other hand, show that all the hydrochloric acid-TBP compounds known are hydrated.

A phenomenon which has so far not been reported was observed in connection with the hydration of the hydrochloric acid species extracted. It was found that a homogeneous equilibrium organic layer, which has already been completely separated from its equilibrium aqueous phase, releases a second layer after a few days. This "spontaneous dehydration" was more closely investigated and the results will be reported in a subsequent paper. All the results presented in this paper are based on measurements carried out on aqueous and organic layers immediately after equilibration.

From the above discussion, the following scheme may be suggested for the interaction of TBP with aqueous hydrochloric acid. At low acidities up to about 3 M initial aqueous HCl, the extraction of acid into the organic phase is probably not accompanied by any interaction between the acid and the TBP. The main reaction in the system up to this point is that of TBP with water. In this region there is only a very slow change, if any, in the physical chemical properties of the organic layer. The swelling of the TBP layer up to this concentration is equal to the swelling caused by its equilibration with water, and neither the viscosity nor the density of the organic phase changes appreciably. The water content of the organic layer remains practically unchanged, and only a minimal amount of acid enters. It could be supposed that the HCl species are appreciably ionized in the monohydrated TBP (although this is not indicated by the calculated degree of ionization) and that only an increase in acid

[21] A. H. LAURENE, D. E. CAMPBELL, S. E. WIBERLEY and H. M. CLARK, *J. Phys. Chem.* **60**, 901 (1956).

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concentration will promote ion-pairing. The occurrence of conductance minima is characteristic of polar compounds dissolved in media of low dielectric constant and has been explained by the formation of ion-pairs.[13,14] This would cause a further rather abrupt increase in the distribution ratio of HCl. On increasing the solute concentration in the initial aqueous solution up to 7 M—i.e. medium concentrations—the dielectric constant of the initial aqueous solution decreases, thus facilitating ion-pair formation. The occurrence of solute–solvent interaction, in addition to interactions of purely coulombic attraction, leads to the stabilization of the ion-pairs formed. At this middle-acidity region, each HCl molecule passing into the TBP carries four water molecules. Thus the water content of the organic layer increases up to a H_2O : TBP ratio of three. When a TBP : HCl ratio of two is reached, accompanied by a change in the physical–chemical properties of the organic layer, the third type of interaction begins. At these high concentrations, the acid passing into the TBP is unhydrated. The water content remains constant, corresponding to a ratio of H_2O : TBP of three, the same as that reached at medium concentrations. At about 10 M acid concentration in the initial aqueous solution, the compound completely formed has a TBP : HCl ratio of one. The formation of this compound is accompanied by a break in the curves showing the dependence of the physical–chemical properties of the organic layer on its acid concentration.

The following reactions are implied in the above arguments:

$$TBP_{org} + H_2O_{aq} \rightarrow [TBP \cdot H_2O]_{org} \quad (1)$$

$$2[TBP \cdot H_2O]_{org} + H^+(H_2O)_{4\,aq} + Cl^-_{aq} \rightarrow [(TBP)_2 \cdot HCl \cdot (H_2O)_6]_{org} \quad (2)$$

$$[(TBP)_2 \cdot HCl \cdot (H_2O)_6]_{org} + H^+_{aq} + Cl^-_{aq} \rightarrow 2[TBP \cdot HCl \cdot (H_2O)_3]_{org} \quad (3)$$

The first reaction shows the formation of the recognized and stable TBP monohydrate.[1,2] The second reaction involves the interaction between this monohydrate and the tetrahydrated hydrochloric acid. The third equation represents the interaction between the first TBP–hydrochloric acid compound and additional unhydrated hydrochloric acid, resulting in the formation of the probable final compound between HCl and TBP.

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 114 to 122. Pergamon Press Ltd. Printed in Northern Ireland

THE SELECTIVE ADSORPTION OF HEXAVALENT URANIUM BY A NON-IONIC PHOSPHORYLATED RESIN FROM SOLUTIONS OF DI-n-BUTYL PHOSPHORIC ACID IN BENZENE

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(*Received* 8 *September* 1959)

Abstract—Uranium is quantitatively adsorbed by the non-ionic phosphorylated resin diethyl polystyrene-methylenephosphonate (EPMP) from 2 per cent solutions of dibutyl phosphoric acid (HDBP) in benzene. Iron (Fe^{3+}), lanthanum, zirconium, niobium, thorium and mixed fission products when present in the HDBP/benzene phase are not adsorbed. Adsorption of uranium from solutions containing the complex $UO_2(DBP)_2 \cdot 2HDBP$ results in the liberation of approximately two equivalents of HDBP and is considered to occur via the mechanism.

$$2EPMP + UO_2(DBP)_2 \cdot 2HDBP \rightleftharpoons UO_2(DBP)_2 \cdot 2EPMP + (HDBP)_2.$$

The uranium is quantitatively eluted with a benzene solution of dimethyl formamide. Under low loading conditions HDBP is adsorbed in the absence of uranium as EPMP·HDBP. The selectivity for uranium is compared with the synergic enhancement of uranium extraction with combinations of non-ionic and acidic phosphorylated solvents.

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MONO-BASIC phosphorylated reagents HX (where $X = (RO)_2P(O)\overline{O}$) are dimeric in inert diluents and extract uranium under low loading conditions as follows,[1]

$$UO_2^{++} + 2(HX)_2 \rightleftharpoons UO_2X_2 \cdot 2HX + 2H^+ \quad (1)$$

A feature of the extraction with these reagents is that in a number of cases a combination of HX and a non-ionic phosphorylated reagent N (were $N = A_3P(O)$ and A is an alkyl or alkoxy group) results in an enhancement of the extraction coefficient such that the latter is considerably in excess of the sum of the coefficients obtained with the separate reagents.[2] With the possible exception of neptunyl and plutonyl ions this synergic effect has not been observed with other metals such as Fe^{3+}, La, V, Mo, Al and Th though the general extraction mechanism with HX alone is the same under low loading conditions as for the uranyl ion.[3,4]

$$M^{n+} + n(HX)_2 \rightleftharpoons MX_n \cdot nHX + nH^+ \quad (2)$$

The effect clearly implies a reaction between the non-ionic reagent N and the extracted uranium and that this reaction is confined to the latter species only. The American workers[2,4,5] who first drew attention to these remarkable features of uranium

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[1] C. F. BAES JR., R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).
[2] J. M. SCHMITT, C. A. BLAKE, JR., K. B. BROWN and C. F. COLEMAN, U.S.Pat. 2 859 004 (1958).
[3] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **7**, 280 (1958).
[4] C. A. BLAKE, JR., C. F. RAES JR., K. B. BROWN, C. F. COLEMAN and J. C. WHITE, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/1550.
[5] C. A. BLAKE JR., D. E. HORNER, and J. M. SCHMITT, ORNL–2259 (1959).

extraction are inclined to favour the following extraction mechanism in the presence of N

$$UO_2^{2+} + 2(HX)_2 + N \rightleftharpoons UO_2X_2{\cdot}2HX \ldots N + 2H^+ \quad (3)$$

with N probably attached through hydrogen bonding in the extracted species. Although experimental evidence is quoted to substantiate this hypothesis,[5] the absence of the synergic effect with most other elements is surprising, as with the same general extraction mechanism (equation 2), one would also expect the formation of the hydrogen-bonded complexes $MX_n nHX \ldots yN$ ($y \geqslant 1$) with other species in the presence of N. Also, experiments of ours have shown that benzene solutions of uranyl dibutyl phosphate [$UO_2(DBP)_2$] and $UO_2(DBP)_2{\cdot}2HDBP$ remain anhydrous after equilibration with aqueous solutions, and this precludes an otherwise likely possibility that the enhanced partitions are the result of water displacement from the complex by the synergising reagent such as

$$UO_2X_2{\cdot}2HXH_2O + N \rightleftharpoons UO_2X_2{\cdot}2HX{\cdot}N + H_2O$$

Considerations such as these and the likelihood of an octa- rather than a hexa-co-ordinated uranium in the species extracted by HX in the absence of N led to the suggestion that the extraction mechanism in its presence may be[6]

$$UO_2^{2+} + (HX)_2 + 2N \rightleftharpoons UO_2X_2{\cdot}2N + 2H^+ \quad (4)$$

and that synergisis resulted from the monomeric N obviating the necessity of dissociation of the relatively stable dimer ($K_{2HX}^{(HX)_2} \simeq 10^6$) which is essential in equation (1). This is also equivalent to saying that the addition of N to a system containing $UO_2X_2{\cdot}2HX$ should result in the reaction

$$UO_2X_2 2HX + 2N \rightleftharpoons UO_2X_2{\cdot}2N + (HX)_2 \quad (5)$$

It is conceivable that the liberation of $(HX)_2$ in this instance could be detected and estimated by physical methods, e.g. infra-red spectroscopy.* However, it was considered of interest to test equations (3) and (5) by substituting a non-ionic phosphorylated resin[7] for N. If uranium is adsorbed in accordance with the following equation [analogous to (5)]:

$$UO_2X_2{\cdot}2HX + 2R \rightleftharpoons UO_2X_2{\cdot}2R + (HX)_2, \quad (6)$$

the liberated acid could be estimated by direct titration of $(HX)_2$ in the inert diluent phase. On the other hand if the adsorption mechanism is analogous to that of equation (3)

$$UO_2X_2{\cdot}2HX + R \rightleftharpoons UO_2X_2 2HX \ldots R \quad (7)$$

the acid as well as the uranium should be depleted from the contacting phase. Irrespective, however, of the use of this approach in providing an indication of the validity of equation (3) or (5), the extreme selectivity of the synergic effect should render possible the use of an insoluble resin phase to adsorb and separate uranium from a host of other metals that are extractable by the acid reagent from aqueous solutions into the liquid organic phase. In the subsequent experiments, with a non-ionic phosphonate resin and solutions of uranyl dibutyl phosphate and dibutyl

* See "Note added in proof" p. 121.

[6] J. KENNEDY, AERE/C/M-369 (1958).

[7] J. KENNEDY, *J. Appl. Chem.* **9**, 26 (1959); J. KENNEDY and H. SMALL, AERE/C/R 1668 (1956).

phosphoric acid (HDBP) in benzene, these expectations were fully realised. Eighty-five to ninety per cent of the HDBP in the species $UO_2(DBP)_2 \cdot 2HDBP$ was liberated into the benzene phase on adsorption of the uranium and most of the remaining acid was probably adsorbed as the species R·HDBP.

EXPERIMENTAL

Preparation of resins

The non-ionic resins experimented on were triallyl phosphate (TAP) prepared by bulk polymerization of the monomer[8], and diethyl polystyrene-methylenephosphonate EPMP [—$\underset{|}{\text{CH}}\cdot C_6H_4\cdot CH_2\cdot P(O)(OEt)_2$—]. This was prepared in accordance with Permutit Co. specifications[9] which are based on the general Arbuzov reaction

$$RX + (R'O)_3P \rightarrow RP(O)(OR')_2 + R'X$$

In order to obtain a completely non-ionic EPMP resin the relative quantities of the reagents differed slightly from those recommended by Permutit and the preparation is described here in detail. Triethyl phosphite $(EtO)_3P$ which was obtained from Albright and Wilsons, Birmingham, was redistilled (b.p. 60°/5 mm) over sodium metal. The latter precaution was taken in order to prevent the distillation of traces of the hydrogen phosphonate $(EtO)_2P(O)H$ which has a comparable boiling point and which would otherwise reduce yields of the phosphonate in an Arbuzov reaction. The distillate (144 g) was added to a crosslinked chloromethylated co-polymer of styrene and divinyl benzene (48 g; 20·3% Cl; 1 per cent nominal divinyl benzene) obtained from the Permutit Co. After standing at room temperature for 2 hr the mixture was heated to reflux of the phosphite (ca. 120°C.) in a nitrogen atmosphere. After 4 hr at reflux the resin had absorbed all the phosphite and that which had not reacted (large excess) was removed by washing with cold acetone on a filter, followed by Soxhlet extraction with refluxing acetone. The yield of dry resin product (73·7 g) was theoretical, based on the chlorine content (20·3 per cent) of the intermediate. The phosphorus content of the resin (10·2 per cent), which also agrees with the theoretical calculated content was determined by wet-oxidizing a weighed portion of the resin (1 g) with nitric and sulphuric acid in a Kjeldahl flask. After most of the sulphuric acid was evaporated, the clear residue (ca. 1 cm^3) was diluted with water and neutralized to pH 3·0 with strong alkali (ca. 10 N), followed by potentiometric titration to pH 10·5 with standard 0·1N sodium hydroxide. The phosphoric acid present was estimated from the standard alkali consumed between the first and second equivalence points. Under these conditions of preparation the resin contained no acidic groups. The benzene regain (grammes of benzene absorbed/gramme of resin), measured as for the toluene regain of polystyrene,[10] was 3·3.

Dibutyl phosphoric acid (HDBP) was obtained as a commercial product (98 per cent purity) from Albright and Wilsons. As it did not contain detectable quantities of other phosphoric acids, further purification was considered unessential. Stock solutions of HDBP/benzene were made up by dissolving weighed portions of the acid in benzene. These solutions were also standardized by potentiometric titration of aliquots of the benzene solution in the presence of water.

Uranyl dibutyl phosphate $UO_2(DBP)_2$ was prepared as described elsewhere.[11] Benzene solutions of this compound with varying concentrations of HDBP were made up by dissolving weighed portions of $UO_2(DBP)_2$ in aliquots of the standardized solutions and diluting with benzene to standard volume. Solutions of ^{95}Zr (containing the ^{95}Nb daughter) and $^{59}Fe^{3+}$ were obtained from the Radiochemical Centre, Amersham. ^{140}La and mixed fission products were prepared by neutron irradiation of 'Specpure' lanthanum nitrate and uranyl nitrate in BEPO. Solutions of the β-active elements in 2% HDBP/benzene were obtained by extracting solutions of the isotopes in nitric acid (0·1 N) with an equal volume of organic phase. ^{234}Th (UX_1) was similarly extracted from an aqueous solution containing uranium (5 mg). The extractions of Fe, La, Zr, Nb, Th and uranium were approximately quantitative. Thirty-five per cent of fission product β-activity was extracted from aqueous solutions after a two-day decay period and from considerations of partition data obtained with individual isotopes the extracted activity would be mainly due to rare earths, molybdenum, zirconium and

[8] J. KENNEDY, E. S. LANE and B. K. ROBINSON, *J. Appl. Chem.* **8**, 459 (1958).
[9] J. R. MILLER, CON/HAR. 64 (1956); Private communication (1959).
[10] K. W. PEPPER, *J. Appl. Chem.* **1**, 124 (1951).
[11] J. KENNEDY and S. S. GRIMLEY, AERE/CE/M-48 (1953).

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niobium. Additional uranium was added to the aqueous solution of fission products prior to extraction, which brought its final concentration in the extractant up to 5 mg/50 ml. The concentration of the other isotopes were less than 10^{-6} M.

Adsorption and partition data

Adsorption of uranium from benzene solutions containing $UO_2(DBP)_2$, in the absence and presence of HDBP, was carried out by shaking weighed portions of the resin (½ g) with the solutions (50 ml). The uranium content of the solution after a specified contact period was measured colorimetrically by estimating the peroxide complex[12] after extraction into an aqueous phase with sodium carbonate. The effect of DBP anion on uranium measurement in aqueous solution is undetectable when the mole ratio DBP/U < 30, but in excess of this a correction term was applied ($< +5$ per cent of the observed estimations), which was based on separate measurements with accurately known DBP/U ratios. The uranium adsorbed on the resin was estimated as the difference between the initial and final quantities in the benzene phase. The distribution coefficient (K_d) is defined as the metal adsorbed by 1 g of resin divided by the metal concentration per millilitre of benzene solution at termination of the contact period. In a number of instances the values of K_d for uranium are not equilibrium values. Equilibrium values of K_d for HDBP between resin and benzene in the absence of uranium were similarly obtained from the depletion of the acid in the benzene phase. The phases in these instances were in contact for 20 hr though equilibrium was attained in less than 3 hr.

Adsorption on resin columns was carried out by passing 50 ml of 2% HDBP–benzene solutions containing the metals through beds of resin (2 g; bed dimensions in benzene 12 cm × 0·9 i.d.), which were swollen in benzene prior to transference to columns. The proportion of metal adsorbed was estimated radiometrically in the case of β-active isotopes, or colorimetrically, as previously described, for uranium.

RESULTS AND DISCUSSION

On the basis of its phosphorus content (10·2 per cent), the theoretical capacity of EPMP for uranyl nitrate is 3·19 milliequivalents (meq) U/g assuming the adsorbed species $UO_2(NO_3)_2 \cdot 2EPMP$. The observed capacity on loading from a uranyl nitrate solution in acetone containing 10 mg U/ml as $UO_2(NO_3)_2$, as described for TAP[7], was 2·9 meq U/g. The theoretical capacity, 3·19 meq/g, is assumed in the subsequent discussion.

It was found that the phosphate ester resin (TAP) had a low uranium uptake ($K_d \leqslant 1{\cdot}5$) under the outlined experimental conditions. On the other hand, the uptake of the phosphonate resin EPMP was appreciable with K_d values of 40 to >600 depending on the experimental conditions. As the sequence of synergic enhancement with monomers is phosphate < phosphonate,[2,4,5] the resin adsorption sequence TAP < EPMP is not surprising. K_d values after 20, 90 and 160 hr contact periods for EPMP are plotted in Fig. 1 as a function of excess HDBP.

As $UO_2(DBP)_2$ in the absence of HDBP is polymeric,[13] the evidently slow rate of attainment of equilibrium under these conditions is largely due to steric hindrance to its penetration through the resin network. This effect has also been demonstrated with large ionic species and sulphonated ion exchangers.[14] As a result of the continuous decrease in molecular size of the polymer as the HDBP to $UO_2(DBP)_2$ ratio is increased,[13] the initial increase in K_d with HDBP is evidently due to an increasing rate of diffusion as the polymeric species is degraded. Except for the low initial HDBP: $UO_2(DBP)_2$ ratios ($<1:1$), equilibrium has been attained at 90 hr, and the subsequent sharp decrease in K_d from a maximum of >600 can be ascribed to increasing competition with the liquid phase HDBP for the uranium. This indicates, as is subsequently

[12] A. A. Smales and E. Furby, AERE/C/R–344 (1950).
[13] T. V. Healy and J. Kennedy, *J. Inorg. Nucl. Chem.* **10**, 128 (1959).
[14] T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.* 1208 (1949); J. A. Kitchener, *Ion-Exchange Resins*. Methuen, London (1957).

confirmed, that liberation of HDBP accompanies the adsorption of uranium. The equilibrium K_d value would remain constant, or change much more slowly with HDBP concentration, if the adsorption mechanism was that of equation (7). K_d values as a function of time are given for three initial HDBP : $UO_2(DBP)_2$ ratios in Fig. 2. These

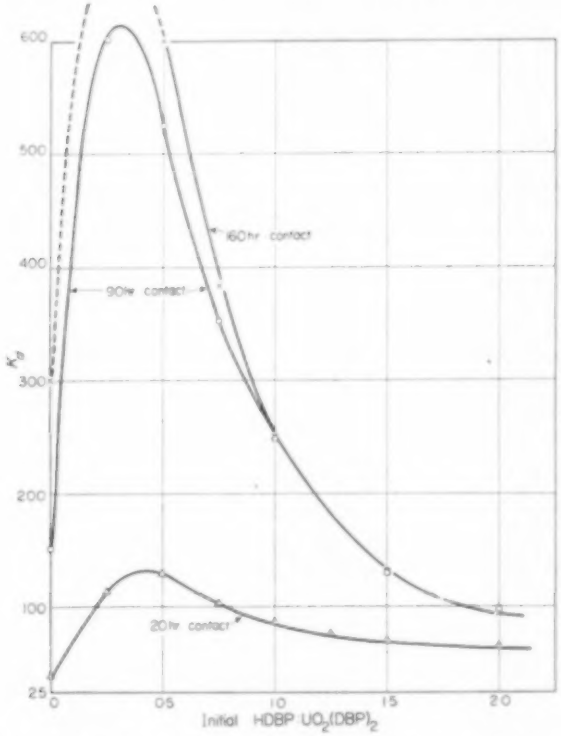

FIG. 1.—K_d values for partition of U (initial conc. = 0·0103 M) between EPMP and HDBP/benzene (50 ml) for varying initial ratio of HDBP : $UO_2(DBP)_2$.

experiments are not exhaustive and were primarily conducted to obtain a practical ratio suitable for subsequent column adsorption experiments.

It is apparent from Figs. 1 and 2 that attainment of equilibrium is relatively slow even for HDBP : $UO_2(DBP)_2$ ratios which are initially as high as 10 : 1, but it is unlikely that the effect in the latter case is the result of the bulky polymeric aggregates of $[UO_2(DBP_2)]$. The quantitative studies of BAES *et al.* on the viscosity and isopiestic properties of dioctyl phosphoric acid and uranium in hexane[1] indicate that the species is largely monomeric at HX : UX_2 ratios equal to or in excess of 2 : 1. Hindrance to diffusion of the species $UO_2(DBP)_2 \cdot 2HDBP$, with a diameter of 16–20 Å, is, however, a likely contributory cause. It has also been observed in the case of complexing resins that attainment of equilibrium in aqueous systems with strongly-bound ions, such as UO_2^{2+}, is extremely slow (> 3 weeks) compared with the weakly-bound alkali and alkaline earth metals under similar conditions.[15] Indications are that this effect may be the result of a surface layer or skin of a stable resin–metal complex which has a

[15] J. KENNEDY, V. J. WHEELER and J. MARRIOT, unpublished work (1959).

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low solvent regain and which presents a barrier to the passage of other ions from the solution phase to the resin interior. An analogous effect with $UO_2(DBP)_2$ and EPMP is a possibility, in view of the considerable contraction of the resin as it is loaded with uranium.

The equilibrium K_d values for HDBP distributed between EPMP and benzene are given in Table 1.

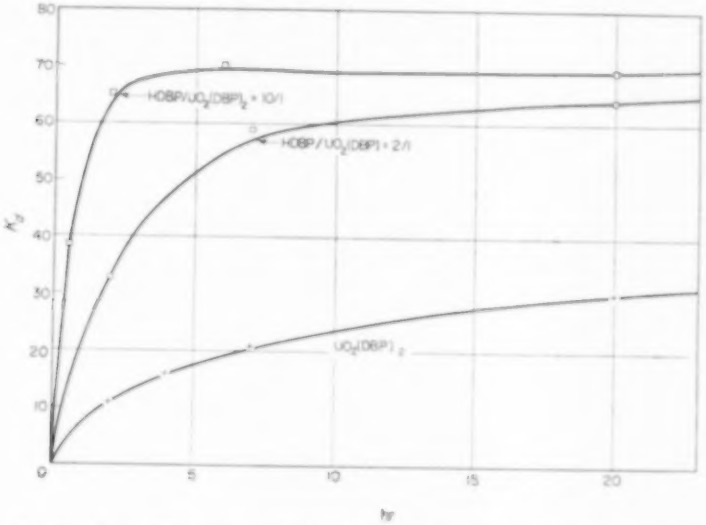

FIG. 2.—Rate of U uptake on EPMP for different initial ratios HDBP : $UO_2(DBP)_2$.

TABLE 1.—DISTRIBUTION AND MASS-ACTION COEFFICIENTS FOR HDBP BETWEEN BENZENE AND EPMP OF THEORETICAL CAPACITY 3·19 meq/g

Final HDBP in solution (meq/ml)	$(HDBP)_0 - \frac{1}{2}HDBP$	HDBP in resin $(HDBP)_R$ (meq/g)	$K_d = \frac{(HDBP)_R}{HDBP}$	$K_c = \frac{R(HDBP)_2}{[(HDBP)_2][R]}$	$K'_c = \frac{[R\,HDBP]^2}{[(HDBP)_2][R]^2}$
0·00153	0·000765	0·0303	20·0	6·2	0·120
0·0044	0·0022	0·0508	13·8	3·6	0·115
0·0107	0·00535	0·0822	7·68	2·4	0·131
0·0286	0·0143	0·1267	4·4	1·4	0·120
0·0642	0·0321	0·1900	3·0	0·95	0·125

Acidic dialkyl phosphates, HX, and non-ionic phosphorylated reagents, N, are known to react as follows.[16]

$$\text{(a) } N + (HX)_2 \rightleftharpoons N \ldots (HX)_2; \qquad \text{(b) } 2N + (HX)_2 \rightleftharpoons 2N \ldots HX \tag{8}$$

and by analogy the adsorption of HDBP by EPMP would be expected to occur via similar reactions. The approximate constancy of K_c' in Table 1 indicates that the predominant mechanism in this instance is equation (8b), and that the adsorbed species is R·HDBP.

[16] H. BAKER and C. F. BAES, Division of Physical Chemistry, 134th Meeting of the American Chemical Society, Chicago (1958).

Potentiometric titration curves of an aqueous phase in contact with HDBP/benzene and in the absence and presence of $UO_2(DBP)_2$ are given in Fig. 3.

HDBP can be readily estimated in the presence of uranium, though a discontinuity occurs after the HDBP has been neutralized due to hydrolysis of $UO_2(DBP)_2$.

Passage of a benzene solution (50 ml) of $UO_2(DBP)_2 \cdot 2HDBP$ (U = 2·35 mg/ml) through a bed of EPMP resin (1·8 g) at a very slow flow rate (passage time 6 hr)

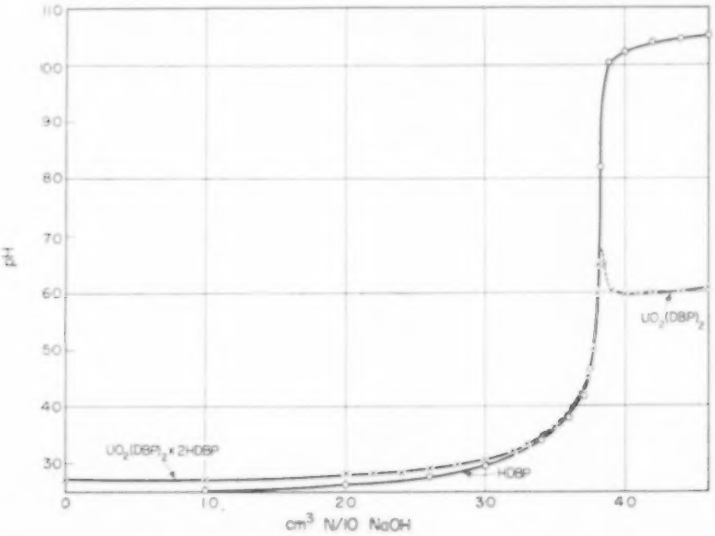

FIG. 3.—Titration of HDBP in benzene ($1{\cdot}96 \times 10^{-2}$ M; 20 ml) with and without $UO_2(DBP)_2$.

resulted in a total adsorption of 90 mg U. Eighty-five per cent of the HDBP initially associated with the adsorbed uranium remained in the benzene phase. Though it is conceivable that some of the remaining acid could be associated with the adsorbed $UO_2(DBP)_2$, all or the largest proportion is adsorbed as R.HDBP, as at least 75 per cent of the original resin capacity (380 mg U) has not reacted with uranium. When a similar experiment is carried out in the absence of uranium, 10 per cent of the total acid is adsorbed. Batch experiments with EPMP ($\frac{1}{2}$ g) and $UO_2(DBP)_2 \cdot 2HDBP$ in 50 ml of benzene led to similar conclusions, with 91 per cent of the HDBP initially associated with the uranium remaining in the benzene phase.

The experiments show almost conclusively that adsorption of uranium results in the liberation of two equivalents of HDBP. As the resin is non-ionic the adsorbed species is predominantly $UO_2(DBP)_2$.

Separation of uranium from other metals

Adsorption of uranium from solutions of 2 per cent HDBP/benzene, when the initial ratio HDBP : $UO_2(DBP)_2 \geqslant 10 : 1$, by columns of EPMP is quantitative. These ratios were chosen so that equilibrium would be rapidly attained (Fig. 2). Under the same conditions no adsorption of Fe^{3+}, La, Zr, Nb or Th occurs. A slight but definite adsorption (ca. 2 per cent) of the β-activity in the fission product extracts occurs after a two-day decay period. No detectable adsorption occurs after 10 days

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decay, which indicates that the adsorbed β-activity may be due to $^{239}NpO_2(DBP)_2$. Uranium is quantitatively recovered by elution of the column with four bed-volumes of a 50% v/v solution of dimethyl formamide in benzene. Partial elution is effected with ten bed-volumes of a similar solution of ethyl alcohol.

CONCLUSIONS

The adsorption of uranium from HDBP/benzene solutions by EPMP occurs via the mechanism

$$x\text{EPMP} + UO_2(DBP)_2{\cdot}2\text{HDBP} \rightleftharpoons UO_2(DBP)_2{\cdot}x\text{EPMP} + (\text{HDBP})_2$$

and can be compared with the adsorption of uranyl nitrate by the non-ionic resin TAP where the adsorbed species is $UO_2(NO_3)_2{\cdot}2TAP$.[7] Though not established in the preceding experiments, x is probably two in the above equation. In all probability a similar reaction such as that depicted in equation (5) occurs with the monomeric non-ionic reagents N, which in turn implies equation (4) as a mechanism of extraction of uranium from aqueous solutions by a combination of acidic (HX) and synergising reagents (N). A first order dependence of the extraction coefficient on the concentration of N when HX is constant, and a second order dependence on the concentration of HX at constant N is quoted as evidence for equation (3).[5] This, however, might perhaps indicate that when HX is in considerable excess of N that the species $UO_2X_2{\cdot}HX{\cdot}N$ is formed which would result in a distribution coefficient that is proportional to $[(HX)_2]^{1.5}[N]$, but would also result in a synergic effect on the same grounds [obviating monomerization of $(HX)_2$] as equation (4)*.

Experimental evidence is accumulating for the octa-co-ordination of uranium and four membered ring structures with bidentate acetate ligands have been demonstrated in sodium uranyl acetate $NaUO_2(O{\cdot}CO{\cdot}CH_3)_3$.[18] Analogous structures with bidentate nitrate ligands were postulated for the complexes of uranyl nitrate with non-ionic phosphorylated reagents,[19] and this has been confirmed by X-ray crystallography in the case of $[(EtO)_3P(O)]_2UO_2(NO_3)_2$.[20] In passing it is of interest to speculate that the enhancement of the extractability of uranium from sulphuric acid solutions into a TBP phase[21] when nitric acid is added to the system is at least partly due to octa-co-ordination being achieved with 2TBP in the anhydrous species 2TBP $UO_2(NO_3)_2$. Assuming a bidentate sulphate, the species 4TBP $UO_2(SO_4)$—whose formation is unlikely as a result of the spatial requirements of the 4TBP molecules—or the hydrated and organo-phobic $(4-x)$TBP xH$_2$O UO_2SO_4 would otherwise be necessary for achieving octa-co-ordination.

Four-membered ring structures involving bidentate DBP and monodentate HDBP ligands in the complex $UO_2(DBP)_2 2HDBP$ are therefore a distinct possibility and could, as previously suggested,[6] explain the causes of synergism in uranium extraction and its absence in the extraction of other metals with combinations of acidic and neutral reagents. It is, however, fair to add that comparisons based on the preceding experiments might lead to erroneous conclusions in view of possible reactions resulting

* *Note added in proof:*—Infra-red examinations of carbon tetrachloride solutions of $UO_2(DBP)_2$, HDBP, and tri-octyl phosphine oxide TOPO, (taken separately and in combination), are consistent with the existence of the species $UO_2(DBP)_2$ 2TOPO and $UO_2(DBP)_2$HDBP·TOPO. No evidence was found for the species $UO_2(DBP)_2{\cdot}2$HDBP . . . TOPO. (J. KENNEDY, P. G. SAMMES and M. DEANE, *Chem. & Ind.* In press.)

[18] W. H. ZACHARIASEN and H. A. PLETTINGER, *Acta Cryst.* **12**, (1959).
[19] J. KENNEDY, *Chem. & Ind.* 950 (1958).
[20] H. LYNTON, Private communication; J. E. FLEMING and H. LYNTON, *Chem & Ind.* 1409 (1959).
[21] T. J. COLLOPY, NLCO–749 (1958).

from the inhomogeneity of the organic phase in the resin/solvent system, and the results obtained are, therefore, considered as supporting rather than conclusive evidence for previous postulates.[6]

Acknowledgements—Our thanks are due to Dr. H. COATES, Albright and Wilsons, Birmingham, and Mr. J. MILLAR, Permutit Co., London, for providing batches of intermediate reagents, and to Dr. H. LYNTON, Fulmer Research Institute, Stoke Poges, for permission to refer to his hitherto unpublished crystallographic analyses. Valuable discussions with Dr. D. DYRSSEN, Royal Institute of Technology, Stockholm, are gratefully acknowledged.

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J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 123 to 147. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

The melting and boiling points of beryllium chloride and an investigation of the NaCl/$BeCl_2$ system

(*Received* 9 *November* 1959)

ONE method at present in use for the production of beryllium metal is the electrolysis of a fused mixture of beryllium chloride with sodium chloride. It was with the object of obtaining data relevant to this process that the work described below was undertaken. References in the literature to the melting and boiling points of beryllium chloride are few and of many years' standing. The most recent and most widely accepted figures are those of RAHLFS and FISCHER[1] who quote 405°C and 488°C respectively—before that LEBEAU[2] had obtained 440 ± 10°C for the melting point, KLEMM[3] had suggested 416 ± 2°C as the most probable value, and SCHMIDT[4] 404°C. The variation in these figures prompted the re-examination.

(1) *The preparation and purification of the chloride.* The material used was prepared in three ways: (a) by the chlorination of a beryllium oxide produced by Murex Ltd. at Milford Haven, (b) by the purification of a crude beryllium chloride produced by Murex Ltd. from (1), and (c) by the chlorination of a commercially available French metal flake (Pechiney).

For (a) the apparatus shown in Fig. 1 was used. Chlorination was achieved by passing carbon tetrachloride vapour with dry argon as carrier gas over the oxide at about 600°C. The chloride formed sublimed and was deposited on the cooler portion of the reaction tube whence it could be removed by tapping. At this stage the product, owing to its highly deliquescent nature, had become slightly hydrated and, owing to the method of removal from the tube, contaminated with beryllium oxide. A very pronounced attack of the hotter end of the furnace tube was observed.

Chlorination of the metal flake at about 600°C was effected with dried and purified cyclinder chlorine in a similar apparatus. The presence of ferric chloride in the initial sublimate was evident, but since its sublimation temperature is much lower than that of beryllium chloride it was possible, by suitable temperature adjustment of the cooler end of the furnace, to move most of it out of the apparatus.

The chloride produced as above and the crude beryllium chloride from Murex were purified in the standard vacuum equipment shown in Fig. 2. Pressures of 20–50 μ and temperatures of 350°–380°C were used in the sublimation procedure and the material when finally purified was sealed off in the third collecting tube. The sealed tubes containing the chloride were subsequently cracked open in a dry-atmosphere glove-box and the material stored in polythene bottles.

The final product was pure white in colour and flowed easily in the sealed tubes without adhering to the walls. A typical spectrographic analysis showed it to contain:-300–400 p.p.m., Fe, 15–30 p.p.m. Mg, 20 p.p.m., Na, 0–20 p.p.m. Other elements were not detected.

When heated above the melting point in a tube open to the atmosphere the material gradually darkened and a black suspension eventually appeared in the melt. In terms of quantity the suspension was $\leqslant$0·1%. It was believed to be largely beryllium oxide caused by hydrolysis and attack on the vessel, a view confirmed by X-ray analysis which identified beryllium oxide and silica but gave no evidence of graphitic carbon. It was assumed, therefore, that the discoloration was due to a trace of amorphous carbon picked up at some stage in the preparation of either oxide or flake and carried forward mechanically during sublimation. This view is supported by the fact that the intensity of the colour decreased with successive sublimations although it was not possible to eliminate it completely.

[1] O. RAHLFS and W. FISCHER, *Z. Anorg. Chem.* **211**, 349 (1933).
[2] LEBEAU, *Ann. Chim. Phys.* **16** (7), 493 (1899).
[3] W. KLEMM, *Z. Anorg. Chem.* **152**, 243 (1926).
[4] J. M. SCHMIDT, *Bull. Soc. Chem.* **39**, 1686 (1926).

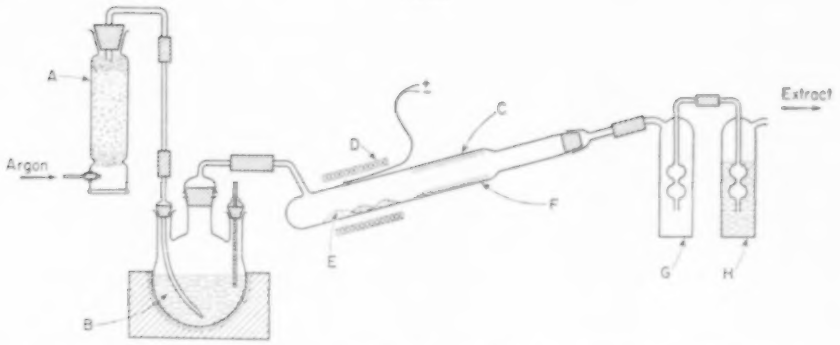

FIG. 1.—The preparation of beryllium chloride. A silica gel; B carbon tetrachloride; C quartz tube; D furnace; E beryllium oxide; F beryllium chloride; G trap; H water trap.

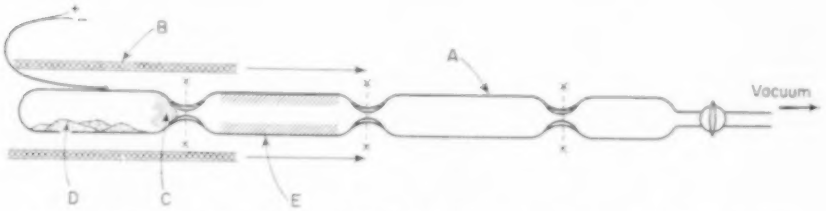

FIG. 2.—The purification of crude beryllium chloride. A Pyrex tube; B furnace; C glass wool; D Crude beryllium chloride; E sublimed beryllium chloride; X sealing off points.

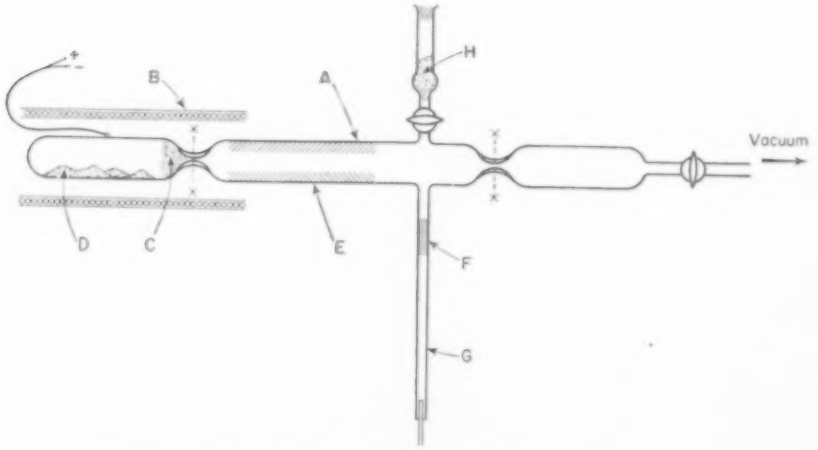

FIG. 3.—The charging of tubes for m.p. and b.p. determinations. A Pyrex tube; B furnace; C glass wool; D pure beryllium chloride; E sublimed beryllium chloride; F suitable graded seal; G m.p. and b.p. tube (various); H phosphorus pentoxide; X sealing off points.

Although attack on the glassware during purification was not apparent, it was not possible completely to sublime a quantity of the chloride. A residue of beryllium oxide always remained indicating that the reaction $2\,BeCl_2 + SiO_2 \rightarrow SiCl_4 + BeO$ occurred at temperatures below 400°C.

(2) *Melting and boiling point determinations.* The apparatus was conventional and consisted of a nichrome-wound furnace surrounded with about four inches of insulating material (vermiculite) placed in a metal beaker. Mild ancillary heating of the outside of the beaker was available so that cooling

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rates could be adjusted as desired. A chromel-alumel thermocouple with a Honeywell-Brown continuous recorder indicated temperatures and the thermal e.m.f. values of the couple were checked against water, sulphur and sodium chloride. In the main, silica tubes were used for the determinations but experiments were also made in nickel, silver and platinum without significant differences in the results.

The design of the tubes and the method of charging with chloride from the vacuum system are shown in Fig. 3. Tubes were sealed off, removed from the system, and opened to atmosphere through

TABLE 1.—THE MELTING AND BOILING POINTS OF BERYLLIUM CHLORIDE

m.p. (°C)	398	403	403	403	399	Average 399·2
	399	395·5	395·5	396·5	396·5	
	396	398	400	400	398	
	401·5	399·5	399·5	401·5	397·5	
b.p. (°C)	481	480	483	483		Average 482·3
	482	583	483	482		
	483	483	482	483		

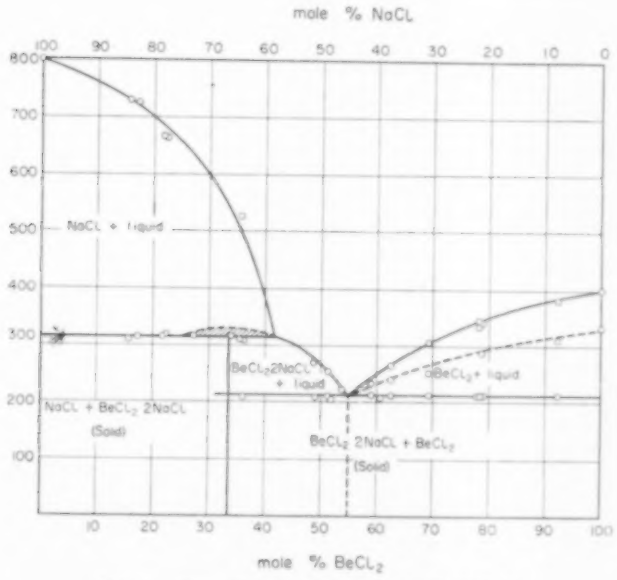

FIG. 4.—Phase diagram for the system NaCl/$BeCl_2$.

the P_2O_5 tube before being placed in the furnace. Rates of cooling averaged approximately 4°C/min.

The results are shown in Table 1.

The recorder was sensitive to a change of 0·04 mV corresponding to 1°C and its accuracy over the range was ±1°C. The standard deviations for the melting and boiling point determinations are ±2·5°C and ±1°C respectively. On the basis of the twenty results presented, and assuming the absence of systematic errors, the mean deviation from the mean is ±1·25°C at the 80% confidence level and the melting point, in round figures, is 399 ± 1°C. The boiling point is 482·5 ± 1°C, the limit imposed by the measuring equipment.

In addition to the halt at the freezing point, a second halt on the cooling curve was observed at approximately 335°C. This represents the transition to a second crystalline form which, under the conditions of the experiment, was not observed on the heating curve.

The sodium chloride/beryllium chloride system

(1) *Determination of the melting points.* With the exception of the tubes the equipment used was as described above. Quartz tubes were employed throughout and the thermo-couple, in a silica sheath, entered the top of the tube instead of the bottom. No P_2O_5 tube was incorporated. The sodium chloride was AnalaR grade and was kept in a hot air oven at 80°–100°C when not in use.

Mixes were prepared in the dry-atmosphere glove-box. With experience it was found possible so to adjust the respective volumes of the dry solids that the resulting composition was fairly close to that desired. They were then shaken to mix the powder as intimately as possible and premelted over a bunsen burner before being placed in the furnace. At the end of each test the quartz tubes were broken open at the bottom and the fused pellet transferred to a weighing bottle for analysis. Care was taken not to include loose sublimate from the upper end of the tubes. The beryllium content of the fusion, after removal of the water-insoluble matter, was determined by precipitation with ammonia. The rates of cooling were similar to those noted in the melting point determinations on beryllium chloride.

(2) *Results.* The results of the determinations are shown in Fig. 4. Except for small differences in detail the general form of the phase diagram is similar to that originally published by SCHMIDT.[4] A eutectic mixture of 55 mol % beryllium chloride was found with a melting point of 210°C as against SCHMIDT's figures of 51 mol % and 215°C. The shaded portion of the curve is hypothetical—the compound $BeCl_2{\cdot}2NaCl$ is unstable in contact with the liquid above its incongruent melting point.

The individual cooling curves showed well-defined arrests along the solidus at 315°C and the eutectic at 210°C. The halts were also clearly evident along both liquidus curves to the left of the eutectic composition. On the beryllium rich side, however, the liquidus arrests near the eutectic composition were less decisive and may be as much as ±10°C in error. Between 70 mol % and 100 mol % beryllium chloride points along the liquidus again became well defined. The points shown within the $BeCl_2$ + liquid area refer to the transition in beryllium chloride at 335°C which is depressed as the proportion of sodium chloride in the mixture increases.

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The reaction between thenoyltrifluoroacetone and its uranyl complex in benzene

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KING[1] has determined the solubility of the uranyl chelate of thenoyltrifluoroacetone (TTA) in benzene solutions of TTA. He expresses his results in terms of an activity coefficient of the chelate, but the deviation of this activity coefficient from unity is so great that he suggests that a soluble addition compound is formed between the chelate and TTA:

$$UO_2X_2 + HX \rightleftharpoons UO_2X_2{\cdot}HX \qquad \text{where HX represents TTA.} \tag{1}$$

It is easy to test this hypothesis using KING's data. If K is the equilibrium constant for equation (1), and if the molecular species are assumed to be ideal solutes, the solubility of the chelate is given by

$$C = S + \frac{QKS}{1 + KS} \tag{2}$$

where S is the solubility in pure benzene and Q is the initial concentration of TTA. The near linearity of the data over a wide range of concentration, as shown in Fig. 1, shows the approximate validity of the assumptions involved in equation (2). From the intercept and slope at low concentration one can calculate a solubility of 0·0096 M for the chelate in pure benzene and $K = 2{\cdot}7$ for reaction (1). The curvature in Fig. 1 at high concentrations shows the picture leading to equation (2) is not exact, and indeed KING and REAS[2] have shown that benzene solutions of TTA are not ideal. Using the value from Fig. 1 for the limiting solubility, using KING and REAS' activity coefficients for TTA, and assuming equal activity coefficients for the two uranium species, one obtains values of K from the measurements at the three higher concentrations of 3·2 in 0·17 M TTA, 3·2 in 0·51 M TTA, and 4·6 in 1·53 M TTA.

[1] E. L. KING, USAEC Report TID-5290 Paper 34, p. 269 (1958).
[2] E. L. KING and W. H. REAS, USAEC Report AECD-2573 (1947).

The high value at the high concentration suggests either non-ideality of the uranium species or formation of a higher complex.

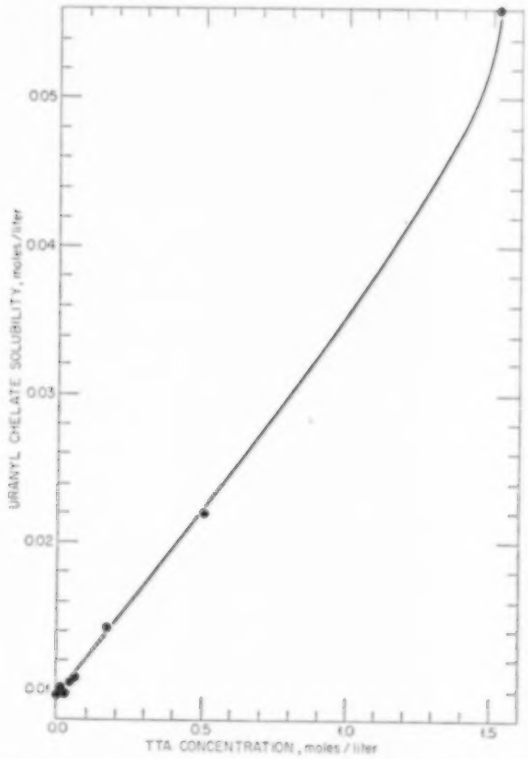

FIG. 1.—Solubility of uranyl TTA chelate in benzene solutions of TTA.

It can be concluded from this analysis that the uranyl-TTA chelate forms an addition compound with TTA in benzene solution, with a formation constant of about 3·2. Solutions containing this complex are not ideal. The existence of this complex is not surprising in view of the many known examples of addition compounds of uranyl chelates.

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Standard substances for magnetic susceptibility measurements

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VERY often $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, "Mohr's salt", is used as a standard substance for the calibration of magnetic susceptibility balances. This salt, recommended in SELWOOD's[1] well-known book, has a gram susceptibility

$$\chi_g = \frac{9500}{T + 1} \cdot 10^{-6} \text{ erg/gauss}^2,$$

according to absolute measurements made by JACKSON.[2]

[1] P.W. SELWOOD, *Magnetochemistry* p. 26. Interscience, New York (1956).
[2] L. C. JACKSON, *Phil. Trans. Roy. Soc.* A **224**, 1 (1924).

A number of difficulties were encountered, however, in using this substance for calibration purposes. First of all, appreciable variations were found in the balance constants when calibrations were carried out at different temperatures. Secondly differences were found when samples of different origin were used. This led to a comparative investigation of the three Tutton salts $MSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ where M = Fe^{2+}, Co^{2+} and Ni^{2+} respectively. In addition a calibration was carried out with ferric-ammonium alum $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$. As a result of this investigation $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ was chosen as standard substance for magnetic susceptibility measurements between 80 and 300° K. It further appeared of importance to have a suitable standard substance in the high-temperature region in order to be able to make very accurate susceptibility measurements between 300 and 1200° K.[3-5]

For several reasons Gd_2O_3 was chosen for this purpose.

Experimental

All susceptibility measurements were carried out with a Faraday torsion balance* in a vacuum case as described in the author's thesis[6] where more complete data may be found. The results of the measurements were represented in terms of the balance constants C as a function of field strength using the known susceptibility-temperature relationships for the various compounds.[2,7]

The balance constants obtained with calibrations at different temperatures or with different substances are compared in Table 1. All results are given as differences in balance constant (ΔC)

TABLE 1

Substance	Origin of sample		Temperature (°C)	ΔC(%)
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Own preparation		20	0
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Own preparation		−193	+1
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Own preparation	recrystallized	20	−1
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Own preparation	recrystallized	−193	+2
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Merck	p.a.	20	−2
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Merck	p.a.	−193	−1
$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$	Own preparation		−193	0
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Merck	p.a.	20	+4
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Merck	p.a.	−193	−8
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Merck	p.a. recrystallized	20	+6
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Merck	p.a. recrystallized	−193	−12
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	AnalaR A.R.		20	−4
$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Own preparation		20	−8
$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Own preparation		−193	−24

The susceptibility-temperature relationships for the Fe^{2+}, Co^{2+} and Ni^{2+}-salts have been given by JACKSON,[2] that for the ferric-ammonium alum by KLEMM.[7]

In the last column: $\Delta C = (C - C_0)/C_0 \times 100\%$ where C_0 = balance constant found by calibration at room temperature with a sample of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ prepared by ourselves. The balance constant C is defined by $U \cdot C = \chi_g \cdot G$ with: U = reading of the torsion balance
G = weight of the sample
χ_g = gram susceptibility of the sample.

relative to the constant obtained by calibration at room temperature with an arbitrary reference sample of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, prepared in the laboratory. The origin of the other samples is indicated in the table.

* Balance and magnet were placed at our disposal by the management of Philips Research Laboratories, Eindhoven.

[3] P. COSSEE, *J. Inorg. Nucl. Chem.* **8**, 483 (1958).
[4] P. COSSEE, *Mol. Phys.* To be published.
[5] P. COSSEE and A. E. VAN ARKEL, *J. Phys. Chem. Solids* To be published.
[6] P. COSSEE, Thesis, Leiden (1956).
[7] W. KLEMM, *Magnetochemie* p. 223. Akad. Verl. Ges., Leipzig (1936).

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In the calibration with Gd_2O_3 (*New Metals and Chemicals*), the balance constants obtained with $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ were used. When the reciprocals of the resulting χ-values were plotted as a function of temperature, a perfectly linear relationship was obtained up to 1070° K. The deviation of each individual point from an ideal Curie–Weiss behaviour did not exceed 0·5%.

Discussion

It is seen from Table 1 that consistent results were obtained for $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ regardless of the temperature of calibration or of the origin of the sample. The remaining fluctuations could be reduced to less than 1·0% by using small uniformly sized crystals.* Moreover, the calibrations with $Fe_2(SO_4)_3{\cdot}(NH_4)_2SO_4{\cdot}24H_2O$ at liquid-air temperature fit remarkably well into those made with $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$.

It is quite obvious from the table that both the Fe^{2+}— and Co^{2+}— Tutton salts are very unsatisfactory as standard substances. It may be theoretically explained why the salts containing Ni^{2+} or Fe^{3+} ions are so much better as standard substances than the salts containing Fe^{2+} or Co^{2+} ions.

Small variations in the composition of the compounds may have an influence on the environment of an appreciable percentage of the magnetic ions. For instance, when $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ contains 5·9 molecules of water instead of 6·0, the error in the chemical analysis is 0·5% only. It may be, however, that 10% of the Fe^{2+} are now surrounded by 5 molecules of water instead of by 6.

It is further known from crystal-field considerations that in sixfold co-ordination Ni^{2+} and Fe^{3+} have a singlet ground level, while Fe^{2+} and Co^{2+} both have three low-lying levels, which makes the magnetic properties of the latter two strongly dependent on the environment.

This possibly explains the sensitivity of the susceptibility of the Fe^{2+}— and Co^{2+}— Tutton salts to recrystallization or to the origin of the sample.

Regarding the choice of Gd_2O_3 as a secondary standard for the calibration at elevated temperatures, the following may be noted:

A standard substance for the high temperature region must be non-volatile and stable against decomposition; valency changes of the magnetic ions and strong ferro- or anti-ferro-magnetic coupling between them are not allowed. Moreover, many magnetic ions show a complicated behaviour at elevated temperatures owing to van Vleck paramagnetism or to the fact that the magnetic moment is no longer constant.

From theoretical considerations it can be concluded that only S-state ions like Mn^{2+}, Fe^{3+} or Gd^{3+} guarantee that Curie's law will be obeyed up to very high temperatures. As Mn^{2+} and Fe^{3+} in oxide lattices may rather easily change their valency and furthermore show strong coupling effects, we have introduced Gd_2O_3 as a standard.

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* A convenient recipe for the preparation of standard $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ is given below: $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ (Merck) is recrystallized; the crystals are crushed in a mortar and small crystals of uniform size (0·3–0·5 mm diameter) are selected by sieving. They must be stored in a desiccator which in its lower part contains solid $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ in equilibrium with the saturated solution in order to maintain the proper vapour-pressure, independently of temperature. The gram susceptibility is then given by[12]

$$\chi_g = \left(\frac{3174}{T + 2{\cdot}5} - 0{\cdot}30\right) 10^{-6} \frac{\text{erg}}{\text{gauss}^2}.$$

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The preparation of 9-tungstoberyllic acid

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Beryllium complexes readily with many oxygenated molecules or anions. Thus it is to be expected that beryllium, which can exist in an oxygenated anion, could complex with the simple tungstate ion

or one of its condensed forms. However, apart from the expected beryllium salts of n, *p* and *m* tungstates, no other compounds are listed in the literature. Beryllium is amphoteric and preliminary experiments suggested some form of complex formation both in alkaline and in acid solutions. In alkaline solution, the spectrophotometric analysis of beryllium using quinalizarin or Eriochrome Cyanine R was found not to be quantitative in the presence of tungstate ion. In an acid solution of beryllium sulphate and sodium tungstate in approximately equimolar proportions, the tungstate ions present exhibited unusual properties. At a pH of 3, if nothing else was present, the bulk of the tungstate could be isolated as the ether addition-compound of metatungstic acid, by the DRECHSEL[1] method. However, with beryllium present in the solution, very little ether addition compound was formed. On concentrating and cooling the solution before the extraction with ether, no precipitate formed, i.e. no paratungstate appeared to be present. Thus the presence of beryllium alters the normal condensation reactions of sodium tungstate on slow acidification. This may be due either to complex formation with the tungstate ion or one or more of its condensed forms, or to the formation of a distinct heteropoly acid. These two mechanisms are not necessarily separate in the initial stages (the formation of heteropoly acids probably involves the combination of the central metal ion with some simple condensed tungstate ion before the formation of the complete heteropoly-acid anion[2]) but only in the final product. The analytical evidence, given later, indicates, because of the condensed form of the anion—nine tungsten atoms and one beryllium atom plus oxygen atoms—that the most likely possibility is the formation of a heteropoly acid.

In the chemistry of most of the higher heteropoly-acids of tungsten, the separation of the pure acid or salts of the acid is difficult. In this case the difficulty was accentuated by the very great solubility of the compound in water and the relative ease of hydrolysis in concentrated solution. The procedure used after the initial acidification involved concentration to precipitate any sodium paratungstate, treatment with ether and 12 N sulphuric acid to remove any *m*-tungstic acid, extracting with amyl alcohol to remove the tungstoberyllic acid and washing the amyl alcohol extract with water to prepare an aqueous solution of the tungstoberyllic acid. This aqueous solution was used in the preparation of the salts. Attempts to isolate the free acid were unsuccessful as some decomposition always took place either on slow evaporation at room temperature or in a heated solution. The sodium, potassium and ammonium salts were very soluble and difficult to prepare in a pure state. Lead and silver gave salts which could be purified by fractional crystallization. However, for ease of analysis, organic salts were usually used to identify the anion.

Polymerized tungstate ions appear to contain octahedral WO_6 groups in the solid phase. In solution, however, the ions are probably heavily hydrated giving a co-ordination number greater than six. The exact nature of these tungstate polymers in solution is doubtful. SPITSYN[3] claims that polymers of a molecular weight corresponding to about fifty WO_4 units are found whereas SOUCHAY[4] finds that the largest ion corresponds to about six WO_4 units. Thus there is some doubt about relating the salts categorized by analysis with the predominant ions in solution. The basicity of tungstoberyllic acid in solution was found by potentiometric titration to be six. This value agrees with the maximum valency found by analysing the salts. The salts were examined thermogravimetrically to determine if possible, differences in the bonding of the water of crystallization. However, the salts began to decompose at about 100–120° C and no apparent break could be observed in the loss of water. The relatively high water contents of the lead and silver salts were not specific as the percentage of water could be varied by altering the conditions of preparation.

Experimental

Fifty-six grammes of sodium tungstate dihydrate were dissolved in about 500 ml of water. The solution was heated almost to boiling. Fifteen grammes of beryllium sulphate in about 200 ml of water were added slowly to the sodium tungstate solution, which was being briskly stirred. At first there was a slight precipitate which gradually redissolved. The solution was then acidified with N sulphuric acid over a period of several hours to a pH of 3, the temperature being kept about 90° C. To remove any sodium paratungstate, the solution was concentrated to about 150 ml and left for a few days. After filtering, ether and 12 N sulphuric acid were added, according to the Drechsel

[1] E. DRECHSEL, *Ber.* **20**, 1453 (1887)
[2] V. I. SPITSYN, *Zh. Neorg. Khim.* **2**, 502 (1957).
[3] V. I. SPITSYN, *Zh. Neorg. Khim.* **2**, 2102 (1957).
[4] P. SOUCHAY, *Ann. Chim.* **18**, 61 (1943).

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method, and the small amount of ether addition-compound of *m*-tungstic acid removed. These two separations accounted for about 10% of the tungsten present. The aqueous layer was warmed gently and a stream of nitrogen bubbled through to remove any ether. It was then extracted twice with amyl alcohol. The amyl alcohol layer was removed and washed with water. The aqueous solution contained about 60% of the original tungsten.

The following salts were prepared and analysed—guanidine, quinine, brucine, cinchonine, pyridine, nitron, lead and silver salts.

Results

Guanidine salt $3(CN_3H_6)_2O{\cdot}BeO{\cdot}9WO_3{\cdot}3H_2O$

	$(CN_3H_6)_2O$	BeO	WO_3	H_2O
Found (%)—(*a*)	15·40	0·96	81·30	2·34
Found (%)—(*b*)	15·76	0·97 0·98	81·45 81·43	1·83
Calc. (%)	15·84	0·95 0·97	81·50 81·10	2·09

Pyridine salt $2{\cdot}5(C_5NH_6)_2O{\cdot}BeO{\cdot}9WO_3{\cdot}3H_2O$

	$(C_5NH_6)_2O$	BeO	WO_3	H_2O
Found (%)—(*a*)	16·40	0·95	81·02	1·63
Found (%)—(*b*)	16·55	0·94 0·94	80·84 80·46	2·05
Calc. (%)	16·87	0·93 0·96	80·20 80·10	2·07

Lead salt $3PbO{\cdot}BeO{\cdot}9WO_3{\cdot}35H_2O$

	PbO	BeO	WO_3	H_2O
Found (%)—(*a*)	20·33	0·70	61·47	17·50
Found (%)—(*b*)	20·21 20·01	0·71 0·70	61·62 61·30	17·46 17·99
Calc. (%)	19·88 19·63	0·72 0·73	61·66 61·18	17·74 18·46

Silver salt $3Ag_2O{\cdot}BeO{\cdot}9WO_3{\cdot}14H_2O$

	Ag_2O	BeO	WO_3	H_2O
Found (%)—(*a*)	21·80	0·81	69·06	8·33
Found (%)—(*b*)	21·55 22·55	0·84 0·85	68·72 69·20	8·89 7·40
Calc. (%)	22·86 22·72	0·82 0·82	68·94 68·23	7·38 8·23

In the cinchonine, quinine, brucine and nitron salts, the amount of organic cation varied from salt to salt, so the ratio BeO:WO_3 only is given.

	$BeO:WO_3$
Cinchonine salt	0·96:9
	0·94:9
Quinine salt	0·98:9
	0·97:9
Brucine salt	0·96:9
	0·96:9
Nitron salt	0·95:9
	0·96:9

Methods

The standard methods of determining the ratio $BeO:WO_3$ proved inapplicable in this case. Tungstic acid could not be completely removed from beryllium hydroxide, precipitated by adding ammonium chloride and ammonium hydroxide, and low and variable beryllium analyses were obtained after removing tungsten by boiling with caustic soda solution. Attempts to develop a spectrophotometric method using quinalizarin or Eriochrome Cyanine R were unsuccessful. These standard methods probably all failed because of complex formation in solution.

The method finally adopted depended on the volatility of tungsten oxychloride to separate the beryllium from the tungsten. The salts used were all organic-base salts. In the case of the lead and silver salts, the inorganic cation was first removed and the anion precipitated with cinchonine hydrochloride. A quantity of the salt was weighed out in a porcelain boat and placed in an ignition tube. The tube was heated and a stream of dry HCl passed through for 6 hr. The tungsten was removed as the volatile oxychloride and condensed in a cold receiving tube. The dry HCl was then turned off and dry air passed through the tube to ignite the carbon from the organic base. These two processes were repeated until the material in the boat was pure white. As the beryllium oxide left was in a finely divided state, it had to be handled out of draughts, and it had to be cooled and weighed out of contact with moist air, since it absorbed water readily.

The tungsten present was estimated by boiling the salt with caustic soda, then acidifying rapidly with concentrated HCl and adding a 10% solution of cinchonine hydrochloride. The precipitate was ignited to WO_3.

Lead was estimated as the chromate and silver by titration with thiocyanate. The organic cations were analysed in the normal manner. The water content was found by difference.

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The valency of ^{208}Tl formed by alpha-decay in aqueous solution

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The recoil following alpha-emission has a very much higher energy than that following most radioactive processes. For this reason it was of interest to look at the possibility of oxidation due to electron loss from radioactive atoms or ions formed by alpha-decay. (Positive charges have also been recognized by physical means in several cases of alpha-decay. This charge sometimes indicates[1] electron loss from the decay product.) A convenient nuclide for this purpose would be ^{208}Tl (ThC″), the daughter nuclide formed by alpha-emission from ^{212}Bi (ThC). However, in this case the situation is complicated by the fact that alpha-emission is followed in a large proportion of disintegrations by emission of a strongly converted gamma-ray of 40 KeV with a half-life of 4×10^{-12} sec. (This process would again tend to increase the positive charge of the ^{208}Tl atom.) Thus the observed chemical processes are mostly the result of a succession of two separate recoils of which the second one may well have the greater influence.

[1] W. Mund, P. Capron and H. Jodogne, *Bull. Soc. Chim. Belg.* **40**, 35 (1931).

It should be realized that Tl^+ is isoelectronic with Bi^{+++} which probably constitutes a major fraction of the parent nuclide. Loss of a single electron from the recoil product would lead to Tl^{++}, the chemical fate of which is unknown to us. It may well transform to Tl^+ by preference. However, if two electrons should be lost, Tl^{+++} would be formed and this would appear in the thallic-ion fraction. The fact that only about one ThC″ nucleus in three ends up in this fraction indicates that the average electron loss due to the nuclear processes cannot be much higher than 1, at least in this example where the daughter atom is a thallium isotope. (That part of the ThC″ is formed as Tl^+ in aqueous solution has already been demonstrated[2] by HAHN.)

Experimental

The ThC solution was prepared from the radioactive deposit of an emanating radiothorium preparation. The radioactive material had been dissolved in nitric acid with lead and bismuth carrier and ThB had been removed by repeated precipitation of lead sulphate. The ThC″ was allowed

TABLE 1.—DISTRIBUTION OF ThC″ FORMED IN AQUEOUS SOLUTION BETWEEN Tl^+- AND Tl^{+++}-FRACTIONS

Separation method	Concentration ratio Tl/Tl^{+++}	Percentage of radioactivity in Tl^+
Extraction	3	71; 69; 67; 73 (average: 70)
Extraction	1/3	63; 67; 66; 65 (average: 65)
Precipitation	3	77; 71 (average: 74)
Precipitation	1/3	71; 74 (average: 72)

to grow in the solution containing Tl^+ and Tl^{+++} (and nitric and sulphuric acids). After radioactive equilibrium had been reached in this solution between the ThC″ and ThC the latter was precipitated as bismuth phosphate. Two different methods were used for the separation of the ThC″ fractions. The most satisfactory separation consisted of extraction of the thallic fraction by means of hydrochloric acid and ether. In this case both the ether fraction and the aqueous fraction were counted in solution. In the second method thallous ion was precipitated as TlBr and thallic ion as $Tl(OH)_3$. In this case the precipitates were counted. In both methods a scintillation counter was used. It should be specially pointed out that in either method any ThC which might have remained in solution would end up in one of the two thallium fractions and be recognized in the decay curve. Both methods were tested by means of ^{204}Tl (in which case, of course, the counting was done by means of a beta-counter).

From the results in Table I it is seen that we cannot exclude the possibility that the distribution of ThC″ over the monovalent and trivalent thallium fractions depends somewhat on the concentration ratio. A slight influence of the concentration ratio—comparable to that observed—can be explained by exchange during the time required for growth of the ThC″ as was recognized in the experiments with ^{204}Tl. Any influence of the concentration ratio of the thallous and thallic ions on the primary distribution of the radioactivity would involve at most only a very small fraction of the ThC″.

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[2] O. HAHN, *Applied Radiochemistry*. Cornell University Press, Ithaca, N.Y. (1936); see also: J. W. BARNES, W. H. BURGUS and J. A. MISKEL in A. C. WAHL and N. A. BONNER, *Radioactivity Applied to Chemistry* p. 274. John Wiley, New York (1951).

Formation of chloroacetate and bromoacetate ions by recoil processes in solids

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MANY authors have reported the formation of organic radioactive halogen compounds by means of an (n,γ) process on irradiating with neutrons a mixture of an organic liquid and a halogen. We have tried to observe a similar substitution using an (n,α) process, which had the advantage that the target nucleus of the (n,α) process could be incorporated as a cation in the organic solid in the cases of potassium and rubidium acetate. The yield of radiohalogen acetate obtained in this way amounted, however, to a very small fraction of the total halogen produced. This fact led us to carry out some experiments specially designed to explain this observation.

Experimental

The irradiations were performed in the Philips' synchrocyclotron in Amsterdam.

In the first group of experiments potassium acetate and rubidium acetate were irradiated with fast neutrons (for 20 min). After the irradiation carriers of alkali halides, viz. chloride and bromide respectively, and halogenacetate were added to the sample and the mixture dissolved in water. The solution was highly acidified with nitric acid (6 per cent) and silver halide was precipitated by addition of silver nitrate. If the solution is adequately acidified, silver monohalogenacetate will not precipitate. In most experiments alkali halide was added again to the filtrate, and the precipitation of silver halide repeated. After the repeated filtration, alkali hydroxide was added to the filtrate, and by 30 min slight boiling halogenacetate was completely hydrolysed forming alkali halide and glycolic acid salt.[1] On addition of nitric acid and silver nitrate, organic halogen precipitated as silver chloride or silver bromide.

In the second group of experiments sodium monochloroacetate was irradiated for 40 min with neutrons which had been moderated in paraffin. Sodium chloride carrier was added to the samples and the mixture dissolved in water. The quantities of irradiated salt dealt with were approximately equivalent to the carrier quantities. Precipitations were performed as described above.

In the third group sodium monobromoacetate was irradiated with slow neutrons for 50 min and mixed with bromide. In one experiment the mixture was dissolved in water containing CH_2Br_2 and extracted with toluene. In the second experiment CH_2Br_2 was not present during the solution process, but it was added to the toluene used for the extraction. The difference between the two experiments was not significant.

In the fourth group we irradiated bromoacetic acid (with thermal neutrons) and dissolved it in toluene containing CH_2Br_2. This liquid was extracted with water containing NaBr. (In some other experiments the inorganic yield of 4·4 hr ^{80}Br was determined in samples which were dissolved in an aqueous bromide solution, which gave the same percentage yield as that listed in Table 1.)

In the experiments of the third and the fourth group the dibromomethane was hydrolysed by boiling the toluene extract with metallic sodium for 4 hr. After this alcohol was added followed by water and a small excess of nitric acid and silver bromide precipitated in the aqueous fraction.

Samples were counted with a β-counter in aluminium dishes. Corrections for self-absorption were not required because identical quantities of silver halides were counted.

In each experiment one part of the irradiated salt was taken for a sample to be counted simultaneously. Decay curves were drawn for all samples and the activities of different samples in one group of experiments were compared. (In the case of rubidium acetate it is not possible to recognize the bromine activities in the preparations which are counted without a chemical separation. The bromoacetic acid is too hygroscopic to be counted for a long period, for this reason the total activity of ^{82}Br could not be measured in this compound.)

Results and Discussion

In the columns of Table 1 the values of the fraction of the radiohalogen in the halogenacetate, the halide and the dibromomethane are given. The very low retention values for potassium acetate and rubidium acetate compared to the values obtained for sodium monochloroacetate and sodium

[1] G. DALIN and J. HAIMSOHN, *Analyt. Chem.* **20**, 470 (1948).

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monobromoacetate are in agreement with LIBBY's billiard-ball theory;[2,3] because in the pure acetates the radiohalogen atom has only a very small chance to be stopped next to a CH_2-group with which it can react, as most radiohalogen atoms will be stopped by the heavy cation. In the sodium halogen acetates the cation and the halogen compete to stop the radioactive atom, thus providing a reasonable chance for the formation of a radiohalogen substituted acetate. Finally in the bromoacetic acid there is no heavy cation to compete with the bromine in stopping the radioactive bromine and this gives us the highest yield of the substitution-retention.

TABLE 1.—DISTRIBUTION OF RADIOHALOGEN IN NEUTRON-IRRADIATED ACETATES AND HALOGENACETATES

Nuclear reaction	Compound irradiated	Fraction in halogenacetate (%)	Fraction in halide (%)	Fraction in dibromomethane (%)
$^{41}K\ (n,\alpha)^{38}Cl$	CH_2COOK	$1{\cdot}7 \pm 0{\cdot}1$	93	
$Rb(n,\alpha)Br$	CH_2COORb	[~0·7]	[99]	
$^{37}Cl\ (n,\gamma)^{38}Cl$	$CH_2ClCOONa$	15 ± 1	86 ± 3	
$^{79}Br\ (n,\gamma)^{80}Br$ (4·4 hr)	$CH_2BrCOONa$	26 ± 1	66 ± 3	4 ± 1
$^{81}Br\ (n,\gamma)^{82}Br$		19 ± 2	69 ± 1	3 ± 1
$^{79}Br\ (n,\gamma)^{80}Br$ (4·4 hr)	$CH_2BrCOOH$	56 ± 4	29 ± 1	16 ± 1
$^{81}Br\ (n,\gamma)^{82}Br$		[49 ± 1]	[26 ± 1]	[24 ± 0]

The total activity of bromine in CH_2COORb and of ^{82}Br in $CH_2BrCOOH$ being unknown, in these cases percentages are given of the sum of the activities of the different fractions measured.

The sum of the values listed for bromide and bromoacetate in the case of monobromoacetic acid is about 80 per cent. The remaining 20 per cent are to be explained by the formation of CH_2Br_2 (and possibly similar bromine substituted compounds which our analytical technique would not separate from CH_2Br_2), as was observed originally by GLÜCKAUF and FAY.[4] In the case of sodium bromoacetate and the sodium chloroacetate the production of the corresponding methane derivates accounted for a much smaller fraction of the activity and in the case of the chlorine compound this production may even have been entirely absent.

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[2] W. LIBBY, *J. Amer. Chem. Soc.* **69**, 2523 (1947).
[3] L. FRIEDMAN and W. LIBBY, *J. Chem. Phys.* **17**, 647 (1949).
[4] E. GLÜCKAUF and J. FAY, *J. Chem. Soc.* 390 (1936).

A new preparation of titanium(IV) fluoride

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TITANIUM(IV) fluoride has previously been prepared by the reaction of titanium(IV) chloride or titanium metal with hydrogen fluoride,[1] and by the action of fluorine on titanium metal or its

[1] *Gmelins Handbuch der Anorganischen Chemie* System No. 41, p. 287. Verlag Chemie, Berlin (1951).

oxide.[2] We have found that titanium metal reacts readily with chlorine trifluoride to form titanium (IV) fluoride.[3]

Complete conversion of titanium to the fluoride can be effected by a continuous flow of chlorine trifluoride diluted with helium over the metal heated to 350°C, or by introduction of the gas at room temperature, followed by gradual heating to 350°C. The latter modification has the advantage of allowing better control of the reaction rate, produces less etching of the glass reactor, and gives yields of about 55 per cent, compared to about 45 per cent for the direct 350°C reaction.

Experimental

Chlorine trifluoride was passed directly from the tank to a 25 mm glass reactor tube supported in a combustion furnace. Chips of titanium metal, 1 cm or less in length, were spaced at 2–3 cm intervals along a nickel boat open at both ends. Titanium sample weights varied from 6–8 g. For best results chlorine trifluoride was admitted at such a rate as to maintain slight incandescence of the metal. The system was flushed with helium before each run.

The volatilized fluoride was collected in a condensing tube connected to the reactor through a ground joint, and cooled with solid carbon dioxide. Flushing with helium for several hours at room temperature was necessary to insure removal of condensed chlorine trifluoride (b.p. 11·3°C). All subsequent transfers were made in the dry-box at dew points of about −35°C.

The reaction product gave a negative test for chloride and was sublimed under vacuum before analysis or use. A small amount of red material usually sublimed at about 20° below the sublimation point of the titanium(IV) fluoride but disappeared when the sublimation surface warmed to room temperature.

The product was analysed after slow hydrolysis in moist air. Titanium was determined by ignition to oxide after addition of ammonia solution. Fluoride was determined by oscillometric titration with thorium nitrate after separation by distillation.[4]

Found: Ti, 38·4, 38·5; F, 61·2, 61·2, 61·3. Calc. for TiF_4: Ti, 38·7; F, 61·3.

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[2] H. M. Haendler, S. F. Bartram, R. S. Becker, W. J. Bernard and S. W. Bukata, *J. Amer. Chem. Soc.* **76**, 2177 (1954).
[3] Hückel reports the formation of titanium(III) fluoride by the action of chlorine trifluoride on titanium metal in an autoclave. W. Hückel, *Nachr. Akad. Wiss. Göttingen, Math.—physik Klasse* 36 (1946); *Chem. Abstr.* **43**, 6793 (1949).
[4] C. L. Grant and H. M. Haendler *Analyt. Chem.* **28**, 415 (1956).

The $[Mo(CN)_8]^{1-}$ structure

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The main purpose of the present paper is to present some of the simple consequences of the generally accepted theory of the electronic structures of the $[Mo(CN)_8]^{4-}$ ion and of related ions. I shall, however, take this opportunity of making some more general comments on the stability of the $[Mo(CN)_8]^{4-}$ structure. In order to facilitate our subsequent discussion we regard the $[Mo(CN)_8]^{4-}$ structure as a distorted cubic structure. The vertices of a cube may be divided into two interlocking tetrahedral sets; to obtain the $[Mo(CN)_8]^{4-}$ structure from a cubic MX_8 arrangement one set is flattened along a fourfold axis and the other set elongated along the same axis[1] (Fig. 1).

Calculations based on an electrostatic point-charge model show that in a complex of this type the d_{xy} orbital is substantially more stable than any other,[2,3] and this is indeed quite clear qualitatively from Fig. 1. It has been argued that the diamagnetism of d^2 complexes with this structure is due to the

[1] J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.* **61**, 2853 (1939).
[2] J. H. E. Griffiths, J. Owen and I. M. Ward, *Proc. Roy. Soc.* A **219**, 526 (1953).
[3] J. S. Griffith and L. E. Orgel, *Quart. Rev.* **11**, 381 (1957).

pairing of electrons in the d_{xy} orbital and further that the stability of complexes of this type is limited to d^1 and d^2 ions precisely on account of the extra stability of the d_{xy} orbital. These conclusions, while essentially correct, require a good deal of amplification.

Consider an ion with one d electron in the middle of a cube of ligands and suppose that the electron is confined to the d_{xy} orbital. Electrostatic arguments show that the effect of the asymmetric d electron charge density must be to elongate both tetrahedra.[4] At first sight it might seem that this

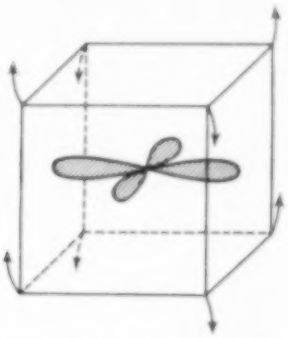

FIG. 1.—Distortion of a cube leading to the $[Mo(CN)_8]^{4-}$ structure. The d_{xy} orbital is shown shaded in the figure.

discrepancy with the $[Mo(CN)_8]^{4-}$ structure could be resolved by taking account of π-bonding, which is important in complex cyanides. Now π-bonding would certainly tend to flatten the tetrahedra since it becomes stronger as the planar configuration is approached. However double-bonding, like electrostatic interaction, affects both tetrahedra equally. There seems to be no simple argument based on the displacement of ligands, one at a time, that leads to the correct structure.

One is forced therefore to the conclusion that it is the interaction between ligands which is responsible for the opposite distortions of the two tetrahedra. Such an interaction may be indirect, through the valency shell of the metal ion,[5] but it is not necessary to assume that this is the only important effect. Thus, if there is appreciable overlap between the ligands of the two tetrahedra then this will be increased by parallel distortions and decreased by opposite distortions. Since in the cubical configuration different ligands of tetrahedra are separated by a distance a where $\frac{1}{2}\sqrt{3}a$ is the metal-ligand distance, while ligands of one tetrahedron are separated by $\sqrt{2}a$, it is clear that the observed structure could come about by distortion of a cube if the inter-ligand repulsive forces increased sufficiently rapidly between internuclear separations of a and $\sqrt{2}a$. For example a "billiard ball" model with the ligand diameter between a and $\sqrt{2}a$ would certainly distort.

The argument so far presented gives no explanation of the restriction of this type of structure to complexes with one or two d electrons. It is well-known that the cube is unstable relative to the square antiprism on purely electrostatic grounds, and the square antiprism structure is indeed found for some eight-co-ordinated complexes of filled shell ions.[6] However, ligand-field arguments which take account of the importance of π bonding do explain why d^1 and d^2 ions are likely to occur with the $[Mo(CN)_8]^{4-}$ structure rather than with the antiprism structure, for it is only in the former that there is an electrostatically stable d orbital capable of forming particularly strong π-bonds. It must be emphasized that the choice between different eight-co-ordinated structures depends on a delicate energy balance and the above argument is merely a rationalization of the facts. The $[Mo(CN)_8]^{4-}$ structure might well occur for a d^0 ion if for stereochemical reasons (polyatomic ligands or crystal packing) the antiprism becomes unstable.

Whatever the reason for the occurrence of the $[Mo(CN)_8]^{4-}$ structure, the following argument still holds. The eight ligands may be divided into two sets of four, one on a flattened and the other on an elongated tetrahedron. The former set are in a region of fairly high d electron density and can

[4] J. D. DUNITZ and L. E. ORGEL, *Advances in Inorganic Chemistry and Radiochemistry* Vol. 2. (In press). Academic Press, New York (1960).
[5] J. W. LINNETT and C. E. MELLISH, *Trans. Faraday Soc.* **50**, 665 (1954).

form strong double-bonds involving the occupied d_{xy} orbital. They are, in fact, in the type of electronic environment characteristically found in metal cyanide complexes. On the other hand the latter set are in a region of low d electron density and can form only weak π-bonds; that is, their environment is more like that in a complex of an A subgroup d^0 ion.

It follows from this that we should expect four of the cyanide groups to be rather easily replaced by non-π-bonding or weakly π-bonding ligands and the other four to be replaceable only by strongly π-bonding groups. We predict therefore that the $[Mo(CN)_8]^{4-}$ arrangement should also be found in compounds MX_4Y_4 where M is a metal ion with one or two d electrons, X is a π-bonding ligand such as CN^-, CO, PR_3, AsR_3, and Y may be a non-π-bonding ligand such as a halide ion, hydroxide ion or saturated amine.

The experimental evidence, while still fragmentary, supports this view. The known octacyanides[6,7] are $[Mo(CN)_8]^{4-}$, $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$, $[W(CN)_8]^{3-}$, $[Re(CN)_8]^{3-}$ and $[Re(CN)_8]^{2-}$, all with 1 or 2 d electrons. The best known substituted compounds are $[Mo(CN)_4(OH)_4]^{4-}$[8] and $[W(CN)_4(OH)_4]^{4-}$[9] and there is no evidence for substitution of more than 4 cyanide groups by other anions. Finally, the compound $[Re(diarsine)_2Cl_4]^+ClO_4^-$ has been prepared and is believed to have a structure related to that of the $[Mo(CN)_8]^{4-}$ ion.[10] Thus in each case there are at least four "double-bonding" ligands in the eight-co-ordinated complexes of d^1 and d^2 ions.

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[6] N. V. Sidgwick, *The Chemical Elements and their Compounds*. Oxford University Press (1950).
[7] R. Colton, R. D. Peacock and G. Wilkinson, *Nature, Lond.* **182**, 393 (1958).
[8] See *Gmelins Handbuch der Chemie* Vol. 17B, System No. 53 (1935).
[9] K. N. Mikhalevich and V. N. Litvinchuk, *Russian J. Inorg. Chem.* **8**, 1775 (1959).
[10] J. E. Fergusson and R. S. Nyholm, *Chem. & Ind.* 1555 (1958).

The processing of iron cyclotron targets in connexion with the Mössbauer effect in ^{57}Fe

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It has been shown that the excitation function for the formation of ^{57}Co by deuteron bombardment of natural iron reaches a rather sharp maximum at a deuteron energy of about 9·5 MeV.[1] In order to facilitate experiments on the Mössbauer effect[2] in the ^{57}Fe 14 keV transition, bombardments were carried out in the Nuffield cyclotron of 1 mm thick targets of spectroscopically pure iron, hard-soldered to water-cooled copper blocks. After activation the surface layer of the iron was removed using a modified "Atlas" 7 in. shaping machine fitted with a specially designed Perspex hopper to collect all the shavings. Experiments were begun using one of these shavings, somewhat reduced in thickness by hammering and rolling.

The remaining shavings (750 mg in a typical run) were dissolved in hydrochloric acid plus a little nitric acid to ensure complete oxidation. The bulk of the iron was removed by solvent extraction with isopropyl ether, and the remaining aqueous solution further treated by ion exchange, using Amberlite IRA 400 and eluting with 6 N hydrochloric acid. The final product solution was substantially free from ^{54}Mn formed by the (d,α) reaction in ^{56}Fe, and contained only about 3 μg of the original iron. The overall recovery of ^{57}Co was over 90 per cent.

To the ^{57}Co solution was added a solution of 10 mg of iron, enriched to more than 99 per cent in ^{56}Fe,[3] dissolved in nitric acid. The combined solution was evaporated to near dryness, and chloride ion was removed by repeated evaporation with nitric acid. The final nitrate solution was made ammoniacal and the solution and ferric hydroxide precipitate evaporated, together, to dryness.

A silica tube was prepared by drawing down one end to a conical shape and sealing it off. A short side-tube was sealed on near this end and drawn down to a fine tip. The active precipitate was transferred to the closed end of the silica tube, and reduced to metallic iron in a current of hydrogen at 600°. The finely divided iron was compacted into the end of the tube and quickly melted in an

[1] W. E. Burcham and C. A. Miller, Private communication.
[2] R. J. Mössbauer, *Z. Physik* **151**, 124 (1958).
[3] The enriched iron isotope was supplied by A.E.R.E. Harwell.

argon atmosphere, using an oxy-coal-gas flame. In this way at least 95 per cent of the ^{56}Fe carrier was recovered as an almost spherical bead. Spectroscopic analysis of a typical inactive bead was kindly carried out for us at A.E.R.E. and showed the presence of 0·3 per cent of silicon. After hammering and annealing the active bead was rolled between nickel sheets to a thickness of about 0·002 in.

Experiments with sources prepared as described, in which the absorption of the 14 keV radiation, in iron absorbers, is measured as a function of the relative motion of the source towards or away from the absorber, show an effect similar to that noted by POUND and REBKA[4,5]. However, the proportion of the radiation emitted without recoil (i.e. in the narrow Mössbauer line) by our source was greater by a factor of about two than that implied by POUND and REBKA's measurements. The reason for this is probably associated with the more uniform distribution of ^{57}Co atoms in the iron lattice, and the negligible self-absorption of the narrow line in a source containing so little ^{57}Fe.

We should like to thank the cyclotron crew for making the bombardments and B. SAUL and J. STRONG for technical assistance.

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[4] N. A. DYSON, P. B. MOON and M. CORDEY-HAYES, In press.
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Determination of the solubility of argon in liquid ammonia by the use of a mass spectrometer

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IN making calculations on the material balance of an ammonia synthesis unit, the solubility data for the system liquid ammonia–ammonia synthesis gas must be known. Precise measurements of

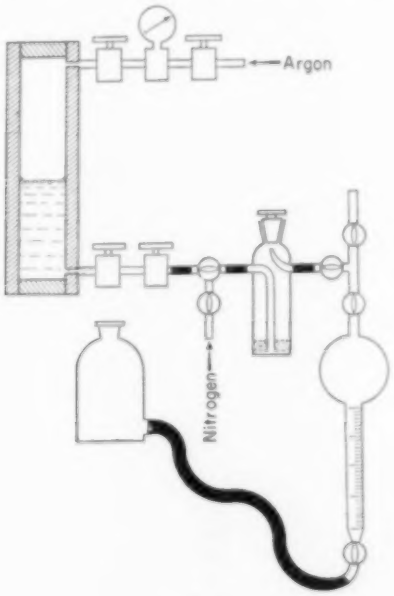

FIG. 1.

the solubility of hydrogen and nitrogen in liquid ammonia were carried out more than twenty years ago.[1] There are, however, still no data available for the solubility of argon and only a few recent measurements, performed in a pilot plant without equilibrium conditions being fulfilled, have been recorded for methane.[2] It was therefore decided to make measurements to obtain the solubilities in liquid ammonia of both these gases in a pressure range up to 100 atmospheres and later of N_2-H_2-A-CH_4-mixtures up to 300 atmospheres. A brief description of the method and the data obtained for pure argon are presented below.

The method used is the static method of solubility measurements, the necessary analyses being performed with a mass spectrometer. From this improvement the difficulties arising from multi-component mixtures, especially from mixtures of argon and nitrogen, are eliminated and, besides, greater sensitivity and speed of measurement are secured. The equilibrium of the liquid and gas phase was established in a high pressure vessel, containing ca. 0·8 l. liquid ammonia and nearly the same volume of the gas investigated, i.e. argon in this series of experiments. The sample was taken from the liquid phase after several hours shaking and then expanded into a gas burette through a solution of sulphuric acid (Fig. 1); the change of the titre of the latter served for the determination of the quantity of ammonia. The whole of the argon liberated from the expanded sample was forced into the burette by a stream of a "neutral" gas, nitrogen in this case. (Before making a measurement, the air was expelled from the whole system by nitrogen.) The volume and temperature of the gas mixture in the burette was measured at barometric pressure which was also determined. The mass spectrometric analysis was then carried out to determine the argon content.

The purity of the argon and nitrogen used and that of the ammonia, too, was controlled by the use of the mass spectrometer. For the future it is planned to carry out the complete analysis of the sample (including ammonia) mass spectrometrically, making use of a heated inlet system to the spectrometer.

TABLE 1

Total pressure (atm)	Number of measurements	Solubility in N cm³ A/g NH_3
25	8	3·58
50	2	8·69
75	5	13·10
100	6	18·20

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The results obtained for argon are presented in Table 1. The solubility data are given, for total pressure and room temperature, in N cm³ A/g NH_3. To demonstrate the reproducibility of the results the data of measurements for 100 atmospheres are presented in Table 2 in detail.

TABLE 2

Total pressure (atm)	Measured value	Deviation from average	
		Abs.	%
100	18·00	0·20	1·09
	18·21	0·01	0·05
	18·51	0·31	1·66
	18·22	0·02	0·10
	18·35	0·15	0·82
	17·91	0·29	1·59
average	18·20		0·88

[1] R. WIEBE and T. H. TREMEARNE, *J. Amer. Chem. Soc.* **55**, 975 (1933).
[2] V. J. ATROSCSENKO and N. A. GAVRJA, *Zh. Prikl. Chim.* **32**, 99 (1957).

The reliability of our method was controlled by a series of measurements on the solubility of nitrogen in ammonia. A very good agreement with the results obtained by WIEBE and TREMEARNE[1] has been found.

The ratio of the solubilities of argon and nitrogen in ammonia as calculated from our laboratory results agreed rather well with the statistical average obtained from measurements carried out previously in the working synthesis unit.[2]

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[2] I. CORNIDES, K. CSEKÖ-CSÁKY and GY. CSEKÖ, *Magy. Kém. Folyóirat* **65**, 358 (1959).

A new metal chloride synthesis

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WE wish to report that iron(III) chloride, niobium(V) chloride, and molybdenum(IV) chloride can be prepared in quantitative yields by refluxing excess hexachlorobutadiene saturated with chlorine over the appropriate metal oxide.

The quantities used by us are 2·0 g of metal oxide in 30 cc of hexachlorobutadiene-1,3, but we see no impediment to larger scale preparations. The amount of hexachlorobutadiene-1,3 is such that there is enough for refluxing, for reacting with the metal oxide, and for dissolving the metal chloride product. The apparatus consists of a 50 ml round-bottom flask fitted with a 300 mm water cooled condenser by means of a T 24/40 ground glass joint. A length of 2 mm capillary tubing enters the flask through a side tube and almost touches the bottom of the flask. A tube containing "Drierite" is fitted to the upper end of the condenser. The flask is heated by means of a Glas-col heating mantle.

The metal oxide is placed in the flask and the apparatus is purged with nitrogen at room temperature. Hexachlorobutadiene-1,3 is added, and chlorine is bubbled through the solution at such a rate that the liquid in the flask does not back up in the capillary tubing between bubbles by more than 3 mm. Refluxing is started and is continued until all of the metal oxide disappears, i.e. 18–24 hr. The apparatus is allowed to cool with chloride gas flowing. At room temperature the apparatus is purged with nitrogen to expel chlorine and phosgene. After replacing the side tube and the condenser with stoppers the flask is removed to an efficient dry box for opening. The metal chloride is filtered and washed with carbon tetrachloride.

Iron(III) *chloride*. After 24 hr of refluxing the flask contains a clear red solution. Upon cooling dichroic red and green platelets form leaving a light yellow solution. The losses in yield are manipulative in addition to that due to a very slight solubility in cold hexachlorobutadiene-1,3. (Found: Fe, 34·52; Cl, 65·51; Cl/Fe, 2·99. Calc. for $FeCl_3$: Fe, 34·43; Cl, 65·57.)

Niobium(V) *chloride*. After 18 hr of refluxing the flask contains a clear orange-red solution. Upon cooling lemon yellow crystals form leaving a light yellow solution. (Found: Nb, 34·26; Cl, 65·49; Cl/Nb, 5·01: Calc. for $NbCl_5$: Nb, 34·38; Cl, 65·62.)

Molybdenum(IV) *chloride*. Molybdenum(IV) oxide starting material was prepared by the reduction of molybdenum(VI) oxide with ammonia.[1] After 24 hr of refluxing the flask contains a clear blood red solution. Upon cooling dark crystals form, but the solution remains highly coloured. It is felt that the molybdenum(IV) chloride has a considerable solubility in both hexachlorobutadiene-1,3 and carbon tetrachloride. The wet crystals (wet with CCl_4) are brown-red; the dry crystals are steel blue. (Found: Mo, 40·23; Cl, 59·95; Cl/Mo, 4·03. Calc. for $MoCl_4$: Mo, 40·35; Cl, 59·65.)

The method offers a major advantage over the sealed tube method.[2] The apparatus required is very simple, assembled of stock items available in any chemical laboratory. It suffers from the disadvantage of limited application. Attempts to apply the method to the oxides of beryllium, aluminium, chromium(III), zinc, zirconium, molybdenum(VI), lanthanum, tantalum, and tungsten (VI) result in partial or no conversion. However the obvious implications of potential metal separation procedures is of at least as much interest as the preparations themselves. The present experiments

[1] G. BRAUER, *Preparative Anorganische Chemie* p. 1054. Fedinand Enke Verlag, Stuttgart (1954).
[2] K. KNOX *et al.*, *J. Amer. Chem. Soc.* **79**, 3358 (1957).

cover a limited set of conditions only. Further studies are under way on the effect of the same and similar chlorocarbons upon various metal oxides.

The method is unique for pure molybdenum(IV) chloride. Previously reported preparations of molybdenum(IV) chloride were all sealed tube reactions, and there was always partial disproportionation of molybdenum(IV) chloride into molybdenum(III) chloride and molybdenum(V) chloride.[2,4,5] The product of this method dissolves completely in water to give a clear, amber solution, indicating the absence of molybdenum(III) chloride inasmuch as the latter is a dark red crystalline powder, insoluble in water. It is surprising to us that what must be molybdenum(IV) chloride dissolved in hexachlorobutadiene-1,3 is not further oxidized by the stream of chlorine at the reflux temperature of the solvent (215°).

Acknowledgement.—We wish to express our appreciation to the Diamond Alkali Company for a gift of a sample of hexachlorobutadiene-1,3.

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[2] E. R. Epperson, *The Synthesis of Anhydrous Metal Chlorides.* Thesis, Chapel Hill, N.C., University of North Carolina (1957).
[4] A. Michael and A. Murphy, *Amer. Chem. J.* **44**, 365 (1910).
[5] H. Remy, *Treatise on Inorganic Chemistry* Vol. II, p. 164. Elsevier Publishing Company, New York.

Inorganic salts dissolved in non-aqueous and in mixed solvents—VI

Studies of two layer formation in the system: $SnCl_4 \cdot 5H_2O$–methanol–carbon tetrachloride

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Optically transparent $SnCl_4 \cdot 5H_2O$–methanol–carbon tetrachloride solutions become opaque, and then separate into two layers on the addition of carbon tetrachloride.[1,2] The amount of carbon tetrachloride required to make a particular solution opaque depends on the initial salt and methanol concentrations for a fixed temperature.

Here are reported detailed studies at 15°C of the composition of $SnCl_4 \cdot 5H_2O$–methanol–carbon tetrachloride solutions at the "Opaque Point" (where one drop more of carbon tetrachloride will yield an opaque solution) and at the stage where there are two clear layers due to the addition of more carbon tetrachloride. Conductance measurements at 25°C are reported for each solution obtained at 15°C by the method outlined. The addition of sufficient methanol will make a clear, single phase system of any "Opaque" or two phase system.

Results and Discussion

In Table 1 are given compositions for selected samples of solutions at the "Opaque Point" and of the two layers obtained on addition of a further 50 ml of carbon tetrachloride. Data for more than eighty samples of different concentrations have been recorded. In addition, a large number of these were checked with duplicate samples. Physical measurements were reproducible to within 1 per cent. Tin and chloride analysis (Lessens' Method as modified by Baker[3] and Fajan's adsorption indicator method[3] respectively) were done in duplicate for each solution. For carbon tetrachloride-rich solutions the analysis values were reproducible to better than 2 per cent; and for the predominantly methanol solutions reproducibility was better than 0·5 per cent.

In computing the SnO_2 concentrations, we have assumed that all the chloride is present as stannic chloride and the "extra tin" is present as SnO_2. The presence of oxychlorides will fit into this scheme.

With basic chlorides present the water concentrations in the methanol-rich solutions given in

[1] M. M. de Maine and P. A. D. de Maine, *J. Inorg. Nucl. Chem.* **11**, 13 (1959).
[2] P. A. D. de Maine, M. M. de Maine and G. E. McAlonie, *J. Inorg. Nucl. Chem.* **14**, In press (1960).
[3] N. H. Furman, *Scott's Standard method of Chemical Analysis* (5th Ed.). D. van Nostrand, New York (1939).

TABLE 1.—VOLUME AND COMPOSITION DATA FOR SINGLE PHASE SOLUTIONS AT THE "OPAQUE POINT" AND FOR EACH OF THE TWO PHASES AFTER THE ADDITION OF A FURTHER 50 ml OF CARBON TETRACHLORIDE

Here are given values for only a small fraction of the total number of solutions for which data were recorded.

	Single phase system at "Opaque Point"								Methanol layer of two-phase system							Carbon tetrachloride layer of two-phase system						
Soln	Volume (ml)	Salt conc. (M)	Sn conc. (M)	Cl conc. (M)	SnO_2* conc (M)	H_2O** conc. (M)	Methanol conc. (M)	Volume of carbon tetrachloride (ml)	Volume (ml)	Sn conc. (M)	Cl conc. (M)	SnO_2* conc. (M)	H_2O*** conc. (M)	Methanol conc. (M)	CCl_4 conc. (M)	Volume (ml)	Sn conc. (M)	Cl conc. (M)	SnO_2 conc. (M)	H_2O conc.**** (M)	Methanol conc. (M)	CCl_4 conc. (M)
1	64·6	0·790	0·772	2·994	0·024	4·355	16·42	14·6	60·5	0·830	3·312	0·002	4·629	22·26	1·03	54·5	0·0033	0·0120	0·0003	0·0165	1·02	9·96
2	65·7	0·746	0·729	2·826	0·022	4·109	16·25	15·7	61·0	0·806	3·005	0·054	4·426	21·80	1·22	55·0	0·0039	0·0120	0·0006	0·0196	0·67	10·12
3	67·1	0·700	0·685	2·654	0·021	3·859	16·04	17·1	61·5	0·744	2·852	0·031	4·210	21·68	1·28	55·5	0·0040	0·0128	0·0008	0·0202	0·94	10·02
4	68·6	0·655	0·640	2·482	0·020	3·610	15·79	18·6	62·5	0·735	2·760	0·046	3·962	21·12	1·51	56·5	0·0049	0·0150	0·0011	0·0243	1·03	9·96
5	70·1	0·612	0·598	2·318	0·019	3·370	15·55	20·1	63·0	0·631	2·530	0·000	3·750	20·67	1·71	57·0	0·0054	0·0181	0·0009	0·0270	1·56	9·74
6	72·2	0·566	0·553	2·143	0·017	3·116	15·20	22·2	64·0	0·644	2·422	0·038	3·515	19·77	2·07	58·5	0·0059	0·0209	0·0007	0·0297	1·62	9·70
7	74·6	0·520	0·508	1·971	0·016	2·867	14·82	24·6	64·5	0·561	2·223	0·006	3·315	19·84	2·04	60·0	0·0073	0·0258	0·0008	0·0364	1·89	9·59
8	77·4	0·468	0·464	1·798	0·014	2·615	14·36	27·4	65·3	0·542	2·070	0·024	3·099	19·18	2·41	63·0	0·0084	0·0264	0·0019	0·0418	2·04	9·53
9	81·2	0·427	0·415	1·592	0·017	2·423	13·73	31·2	66·0	0·504	1·962	0·014	2·981	18·45	2·62	64·5	0·0089	0·0328	0·0007	0·0445	1·81	9·64
10	94·6	0·313	0·303	1·165	0·012	1·773	11·99	44·6	70·0	0·402	1·556	0·010	2·387	16·34	3·51	74·0	0·0173	0·0635	0·0014	0·0863	3·60	8·88
11	98·9	0·279	0·270	1·038	0·011	1·579	11·54	48·9	69·0	0·369	1·441	0·013	2·263	15·73	4·41	80·0	0·0187	0·0656	0·0023	0·0937	2·91	9·18
12	90·0	0·227	0·220	0·845	0·009	1·286	10·21	50·0	50·0	0·359	1·405	0·009	2·314	15·70	3·79	89·0	0·0222	0·0827	0·0015	0·1112	3·58	8·88
13	70·2	0·209	0·203	0·780	0·008	1·187	9·85	40·2	32·0	0·386	1·483	0·008	2·604	16·28	3·56	89·0	0·0202	0·0736	0·0018	0·1011	3·54	8·89
14	73·5	0·153	0·148	0·569	0·006	0·866	7·83	48·5	20·0	0·394	1·578	0·016	3·183	17·11	3·19	114·0	0·0200	0·0699	0·0023	0·0998	3·04	9·11
15	85·1	0·120	0·116	0·447	0·005	0·680	6·86	60·1	15·2	0·425	1·590	0·000	—	—	—	120·0	0·0205	0·0748	0·0018	0·1024	3·35	8·98
16	95·4	0·086	0·083	0·319	0·003	0·458	5·47	73·2	8·2	0·458	1·763	0·028	—	—	—	137·0	0·0190	0·0684	0·0019	0·0951	2·96	9·15
17	91·3	0·067	0·065	0·250	0·003	0·381	4·87	72·5	3·0	—	—	0·018	—	—	—	135·0	0·0163	0·0632	0·0005	0·0816	3·02	9·12

* Sn conc. minus (chloride conc./4) = SnO_2 conc.

** H_2O conc. $= \dfrac{(\text{salt conc.} \times 350{\cdot}61) - 259{\cdot}50\ \text{Cl conc.} - 150{\cdot}7\ SnO_2\ \text{conc.}}{18{\cdot}016}$

*** All water present is assumed to be concentrated in the methanol layer

**** Water conc. is five times the Sn conc.

Table 1 would be about 5 per cent too high. As the solutions have infinite pH values, no hydronium ions are present. Thus it is unlikely that basic chlorides are present. The methanol and carbon tetrachloride concentrations were calculated from density values and salt concentrations. In separate experiments we have found that there is no measurable increase or decrease over the additive volumes for any solution studied.

We have also assumed that the water:tin concentration ratio cannot be greater in the carbon tetrachloride-rich layer than the ratio in the methanol-rich layer.

In Table 2 are given specific and molar conductances for the "Opaque Point" solutions and the methanol-rich layers given in Table 1. Resistances for all predominantly carbon tetrachloride layers exceeded one million ohms (cell constant 0·1106) and thus could not be measured accurately with our Cambridge Radio Co. Impedance Bridge.

TABLE 2.—MOLAR AND SPECIFIC CONDUCTANCES FOR SOLUTIONS AT THE "OPAQUE POINT" AND FOR THE METHANOL-RICH LAYER OF THE CORRESPONDING TWO PHASE SYSTEM

The Sample Numbers in this table refer to the corresponding systems for which data are given in Table 1.

Sample no.	Specific conductance × 10,000		Molar conductance	
	"Opaque Point" solution	Methanol-rich layer	"Opaque Point" solution	Methanol-rich* layer
1	4·39	4·68	55·5	56·4
2	4·01	4·45	53·7	55·2
3	3·82	4·20	54·5	56·5
4	3·52	3·94	53·7	53·5
5	3·19	3·65	52·1	57·8
6	2·91	3·39	51·4	52·7
7	2·58	3·11	49·6	55·4
8	2·28	2·82	48·8	52·0
9	2·01	2·62	47·1	52·0
10	1·22	1·86	39·0	46·1
11	0·91	1·70	32·7	46·1
12	0·70	1·57	31·0	43·7
13	0·59	1·69	28·3	43·7
14	—	1·72	—	43·8
15	—	1·70	—	39·9
16	—	1·95	—	42·6
17	—	—	—	—

* Molar conductance = 1000 specific conductance/Sn conc.

Data show that the concentration ratio, Cl/Sn, is independent of the solvent composition for each kind of solution. Average values for solutions at the "Opaque Point" and the methanol-rich and carbon tetrachloride-rich layers, with square root-mean-square deviations in parentheses, are: 3·86 (0·03); 3·83 (0·06); and 3·45 (0·17) respectively. This suggests that the small amounts of oxychlorides or double salts in the one phase system, are preferentially extracted into the carbon tetrachloride layer. This view is partially supported by the enrichment of the carbon tetrachloride layer with SnO_2 (Table 1).

Tin chloride, and methanol concentrations in the methanol-rich phase are significantly increased from those in the single phase system at the "Opaque Point". Thus two layer formation leads to extraction of carbon tetrachloride by the carbon tetrachloride-rich layer (Table 1). This extraction of carbon tetrachloride is also reflected in the significant increase in molar conductance (Table 2).

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The amount of carbon tetrachloride extracted is increased by adding more carbon tetrachloride to the two-phase systems. The concentrations of methanol, tin, and chloride in the carbon tetrachloride-rich layer, obtained by adding 50 ml of carbon tetrachloride to a solution at the "Opaque Point" increases as the initial salt concentration is lowered. This means that the extraction coefficient (components in CCl_4 layer/components in methanol layer) actually increases as the total salt concentration is decreased. Simultaneously the concentration of carbon tetrachloride in the methanol-rich layer is increased.

A plot of the specific conductance versus the salt concentration at the "Opaque Point" is defined by the linear relation, specific conductance $= 0{\cdot}120 + 0{\cdot}65 \times 10^{-4}$ salt conc. A plot of the corresponding methanol concentration versus the salt concentration gives a monotonic increasing curve (Fig. 1).

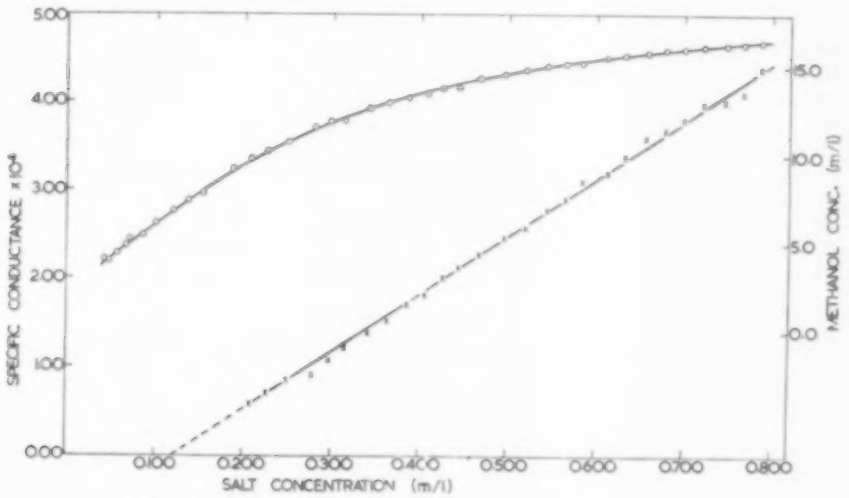

FIG. 1.—Plots of the methanol concentration (—O—), and specific conductance (—X—) vs. salt concentration in solutions at a 15°C "Opaque Point". Resistances were measured at 25°C.

For the methanol-rich layers formed by adding 50 ml of carbon tetrachloride to "Opaque Point" solutions containing 50 ml of salt-methanol solution, there exists a linear relation between the tin concentration and the specific conductance thus:

Specific conductance $= 0{\cdot}069 + 0{\cdot}61 \times 10^{-4}$ tin conc. Plots with the corresponding methanol concentration again define a monotonic increasing function.

These data do suggest that specific interactions between tin(IV) species and the methanol molecules actually prevent miscibility with carbon tetrachloride.

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The preparation of mononitratodioxovanadium(V), VO_2NO_3

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THE recent series of papers by ADDISON and his school[1] concerning anhydrous liquid dinitrogen tetroxide as a preparative solvent for metal nitrates prompted an attempt to prepare a nitrate of

[1] C. C. ADDISON *et al.*, *J. Chem. Soc.* S211, S218 (1949); 1289, 1294, 1298, 1303, 2829, 2833, 2838, 2843 (1951); 1390, 1399, 4079 (1952); 1319, 1869, 1874, 2631 (1953); 1138, 1143 (1954); 1941, 2705, 2709, 3900 (1956); 3099 (1958).

vanadium. Vanadium nitrates are unknown in the solid state, but they are believed to exist in decinormal solutions of vanadium in strong nitric acid.[2] The exact species in which vanadium occurs in these solutions is not definitely known, but it is hypothesized that it is present as either $VO(NO_3)_3$ or VO_2NO_3, both of which are possible in strongly acidic solutions.

A solid, brick-red, free-flowing oxynitrate of vanadium which corresponds to the formula VO_2NO_3 has been prepared by the reaction of chips of electrolytic vanadium with excess liquid dinitrogen tetroxide at 0°C using an acetonitrile catalyst according to the equation:

$$V + 2N_2O_4 \xrightarrow[0°C]{CH_3CN} VO_2NO_3 \uparrow + 3\,NO \uparrow \qquad (1)$$

The choice of acetonitrile as the catalyst was one of convenience, and it is one of the electron donor catalysts described by ADDISON.[1]

The properties of dinitrogen tetroxide have been completely described elsewhere.[1,3,4,5] Dinitrogen tetroxide supplied by the Matheson Company was used for all preparations. The cylinder was fitted with stainless steel couplings and connected to the all-glass apparatus described below. Eastman-Kodak "White Label" acetonitrile was used as the catalyst. Electrolytic vanadium chips prepared by the Union Carbide Metals Company were used as the vanadium source.

The all-glass apparatus consisted of a 250 ml Pyrex three-necked flask fitted with 24/40 $\overline{S}$ female joints. The centre connexion was fitted with a cold-finger condenser which led to a vacuum pump via an intermediate liquid nitrogen trap. One of the side connexions served as the inlet for the dinitrogen tetroxide and argon, both of which were first passed through a calcium chloride tube to ensure anhydrous conditions. The remaining connexion was fitted with a separatory funnel through which the acetonitrile catalyst was added.

A typical preparation involved the following steps: 5 g of peasized electrolytic vanadium chips were placed in the flask and the entire system was purged with dry argon for about 40 min. The flask and cold finger were cooled with ice so that the temperature was maintained at 0 to 5°C during the course of the preparation. Dinitrogen tetroxide (liquid range −9·3 to +21·8°C.) was then introduced into the flask and allowed to liquefy until 75–100 ml of the brownish liquid were present in the flask. Then about 5–8 ml of acetonitrile were added, and a brick-red precipitate formed. The reaction mixture was allowed to stand for 5–6 hr, after which the excess solvent and catalyst were removed under vacuum. The resulting brick-red powder was found to be unstable in moist air and was, therefore, handled in a dry box. The yield was 91 per cent based on vanadium according to equation (1). Chemical analysis gave the following results: Found: V, by the ferrous sulphate method,[6] 35·6% NO_3: by the nitron method,[7] 41·9%. Calc. for VO_2NO_3: V, 35·2%; NO_3, 42·8%.

The product was found to be very soluble in water, producing an orange-coloured solution which, when the concentration was at least 730 mg/100 ml water, formed a deep brown gel within 24 hr of the solution preparation. Less concentrated solutions were stable indefinitely. Exposure of the salt to moist air caused a slow change to a brown gel similar to that described above. The freshly prepared solution gave a positive qualitative test for nitrate with brucine. Attempts to recover the original brick-red powder from aqueous solution proved futile. Rapid evaporation by heating, as well as slow crystallization, produced vanadium pentoxide with loss of nitrate. The brick-red powder was found to be insoluble in the more common organic solvents. Heating the brick-red powder at 350°C either *in vacuo*, or in an argon stream for 6 hr caused decomposition which proceeded via the equation:

$$2VO_2NO_3 \rightarrow V_2O_5 + N_2O_5 \uparrow \qquad (2)$$

The tan powder remaining was found to be vanadium pentoxide by analysis. A solution formed by collecting the evolved gas in distilled water gave a positive qualitative test for nitrate with brucine, indicating that dinitrogen pentoxide or its decomposition products, nitrogen dioxide and oxygen, was the gas and/or gases evolved.

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Qualitative infra-red studies indicate that both nitrate ions and vanadium–oxygen linkages are present in the brick-red powder. MILLER and WILKINS[5] found that ten inorganic nitrates showed common absorptions in the ranges 7·25–7·41 μ and 11·90–12·25 μ when examined in potassium bromide disks. Under the same conditions the monitratodioxovanadium (V) exhibited a very strong absorption at 7·25 μ and a very weak absorption at 12·19 μ, indicating the presence of ionic nitrate. Under identical conditions vanadyl sulphate, ($VOSO_4$); vanadium pentoxide; *bis*-(acetylacetonate)-monoxovanadium (IV), ($VO(acac)_2$); and monoitratodioxovanadium (V) showed common absorptions in the 9·8–10·0 μ range, which is apparently characteristic of the vanadium–oxygen linkage. This has recently been verified.[6] The brick-red powder had a specific gravity of 2·055 at 25°C as determined by the pycnometer method. No diffraction pattern could be obtained, indicating that the compound was amorphous. Examination of the compound under polarized light revealed that it had but one index of refraction (which was greater than 1·78). Therefore, it is isotropic, further evidence of its amorphous character.

The molecular weight of the compound was determined in water at 25°C by the isopiestic method using copper (II) nitrate as a standard and was found to be 150 compared to 144·96 calculated for the formula VO_2NO_3. Only cursory magnetic measurements were made. The compound was found to be slightly diamagnetic at room temperature (25°C) and with a molar susceptibility of $+116 \times 10^{-6}$ c.g.s.u. at liquid nitrogen temperatures (−195°C). The latter figure corresponds to a magnetic moment of 0·08 Bohr magnetons (B.M.) versus the expected zero B.M. for a compound with no unpaired electrons.

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LETTERS TO THE EDITOR

Occurrence and separation of higher polythionic acids in Wackenroder liquid

(*Received* 23 *February* 1960)

We have carried out an investigation of products of the Wackenroder reaction by paper chromatography (Whatman Paper No. 1, solvent mixture n-butanol, acetic acid, acetoacetic ester, water, 10:2:1:7 by volume[1]). We find:

(1) A small amount of Wackenroder liquid obtained by the reaction of hydrogen sulphide and sulphur dioxide in water yielded nine spots on the paper strips after spraying with silver nitrate solution following the chromatographic separation. By means of; (a) determinations of the R_f of the polythionic acids on samples prepared by established methods;[2,3,4,5] (b) determination of x in the formula $H_2S_xO_6$, by dissolving the acid from the paper strips in ether and titrating the $S_2O_3^{--}$ formed by the decomposition of the acid with CN^- and SO_3^{--};[5,6] and (c) U.V. absorption spectra of the $H_2S_xO_6$ dissolved from the paper strips by water; it was found that the products formed in the Wackenroder reaction and separated by paper chromatography are $H_2S_4O_6$ ($R_f = \sim 0{\cdot}15$, diffuse), $H_2S_5O_6$ ($R_f = 0{\cdot}20$), $H_2S_6O_6$ ($R_f = 0{\cdot}25$), $H_2S_7O_6$ ($R_f = 0{\cdot}30$), $H_2S_8O_6$ ($R_f = 0{\cdot}37$), $H_2S_9O_6$ ($R_f = 0{\cdot}45$), $H_2S_{10}O_6$ ($R_f = 0{\cdot}52$), $H_2S_xO_6$ ($x > 10$, $R_f = \sim 0{\cdot}65$, diffuse), H_2S ($R_f = 0{\cdot}90$).

(2) The polythionic acids formed by the Wackenroder reaction in 50 per cent aqueous CH_3COOH are the acids $H_2S_xO_6$, $x = 3$–12, in HCl, 2–10 M, the range $x = 8$–11 is found. The R_f values are recorded above and the acids have been identified by the methods (a), (b), and (c) above.

(3) The first products of the Wackenroder reaction are $H_2S_2O_3$ and $H_2S_2O_6$.

(4) The higher polythionic acids (above hexathionic) undergo decomposition on adding potassium acetate to Wackenroder liquid; as is observed in the Pollard solvent.[7] This is in accordance with the sensitivity of the polythionic acids to hydroxyl ions.[8]

The results of these experiments clearly demonstrate the occurrence of higher polythionic acids in the Wackenroder liquid, the influence of acidity on the reaction, and the possibility of preparation for the first time of pure $H_2S_xO_6$ with $x = 9$ and 11.

The only reaction mechanism which agrees with these results as well as with unpublished radiochemical investigation is the one proposed by van der Heijde,[9] with the assumption that the chain-length in the intermediate is increasing with the acidity.

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Effect of graphite on molten samarium fluoride at elevated temperatures[1]

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The densities of the Group IIA and IIIA fluorides in the molten state were determined by heating these fluorides in a graphite crucible to temperatures above their melting points (1600–2500°K) and

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measuring the loss in weight of an immersed tungsten or molybdenum sinker.[2,3,4] Of the fluorides studied (barium, strontium, calcium, magnesium, yttrium, lanthanum, cerium, praeseodymium, neodymium and samarium fluorides) it was found that only the neodymium and samarium fluorides reacted with the graphite. When molten neodymium fluoride, NdF_3, was heated for 2 hr in a graphite crucible at a temperature ranging from 1700° to 2200°K, about 1·5 per cent of the fluoride was converted into the carbide. None of the other fluorides formed more than 0·1 per cent even when heated to 2500°K.

When samarium trifluoride, a white solid melting at about 1670°K was heated in a graphite crucible, it was reduced to the red-brown difluoride as follows:

$$4\,SmF_3 + C \rightarrow 4\,SmF_3 + CF_4 \text{ (or higher carbon fluorides).}$$

None of the other fluorides were reduced by the graphite. The effects of temperature, time and carbon surface area on percent reduction of SmF_3 to SmF_2 were studied. The conditions used and results obtained are tabulated in Table 1 and show that increases in heating time, temperature and carbon

TABLE 1.—REDUCTION OF SmF_3 TO SmF_2 BY GRAPHITE

Condition	Graphite surface area, (cm^2/g SmF_3)	Wt. SmF_3 (g)	Temperature (°K)	Time (hr)	Reduction (wt. %)
Graphite crucible and tungsten float	0·35	350	1600–1800 1800–2200 2200–2300	1 1½ 1	6·8
Graphite crucible only	0·40	30	1700–2000 2000–2200	1 1¾	16·5
Graphite crucible and 2 g graphite powder	—	100	1550 1550–1700 1700–2110	1 1 2	11·4
Graphite crucible and graphite rods	1·2	100	1600–2080 2080–2300 2300–2380	1 ¾ 4	24·8
Graphite crucible and graphite chips	3·9	116	2175–2250	2	30·3

surface area all tend to increase the percent reduction. The maximum reduction obtained to date is 30 wt. %.

The effects of metals, such as molybdenum and tungsten, on the reduction of the trivalent to the divalent samarium fluoride was studied. It was found that when 100 g of SmF_3 was melted and heated at 2000 ± 25°K for 1–2 hr in a molybdenum crucible (surface area = 50 cm^2) with tungsten wires (surface area = 40 cm^2) inserted into the melt, less than 0·3 wt. % of the trifluoride was reduced to the difluoride. Therefore tungsten and molybdenum under these conditions have little effect on the reduction of SmF_3 to SmF_2.

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BOOK REVIEWS

F. S. MARTIN and G. L. MILES: **The Chemical Processing of Nuclear Fuels.** Butterworths, London; Academic Press, New York, 1958. x + 242 pp., £2; $7.50.

THE nuclear energy industry is now taking shape as the projected nuclear power programmes of Great Britain, U.S.S.R., France and America are being implemented. Hitherto, the atomic energy industry has been centred around the production of fissile material, ^{239}Pu and ^{235}U, for military use and the techniques of processing irradiated fuel rods described at the 1955 and 1958 Geneva conferences are largely based on the aqueous chemical processes necessary for the efficient separation of ^{239}Pu from irradiated uranium.

A great deal of published information has resulted from the Geneva Conferences and it is true to say that more has been published on the processing of nuclear fuels than is customary for new chemical processes. Despite this large volume of published information, there is a need for a critical compilation of the information and an assessment of the problems of chemical processing associated with a nuclear power programme.

MARTIN and MILES survey the problem with the aim of giving a thorough introduction primarily intended for science and engineering graduates.

In Part I of their new volume *Chemical Processing of Nuclear Fuels*, they describe briefly the reasons for fuel processing and relate these to possible fuel cycles, including the one most favoured at the moment in the U.K., a combination of thermal reactors of the Calder Hall and Advanced Gas Cooled types with Pu-fuelled Fast Reactors.

The discussion on the economics of fuel processing in Part I gives figures which must be treated with reserve when considering the costs of processing the irradiated fuel from a large programme such as that of the U.K.

Part 2, *Aqueous Processes* gives a concise and useful survey of the solution chemistry of Th, Pu, U, Np, Pu and Am, whilst the fission products are briefly described in their periodic groups and reference is made to the relevant chemistry of canning and alloying elements.

The section on solvent extraction, which is the major unit process in the present nuclear fuel industry, gives a brief description of the Nernst Partition Law and its application to multiple batch extraction, but the authors fail to give the reader the theory of counter-current continuous extraction systems which are used so successfully. If this had been done, and the extraction behaviour of U, Pu, Ru and Zr described in relation to such counter-current systems, this part of the book would have been of greater value.

Similarly, the section on Technical Solvent Extraction is a very elementary introduction to the broad principles of operation of extraction columns and mixer settlers. It does not give any indication of the design principles or operational characteristics of solvent extraction equipment or of the special problems of processing radioactive liquors.

These two sections of the book compare unfavourably with the treatment accorded to the same subjects by BENEDICT and PIGFORD in their comparable volume *Nuclear Chemical Engineering*.

In the remainder of the section on aqueous processing the authors give concise and well balanced descriptions of the "Butex", "Purex", and "Hexone" solvent extraction processes for unalloyed fuels.

The plutonium purification process using thenoyl trifluoracetone (TTA) as an extractant is described in more detail than is warranted for an obsolete process.

Part 2 also contains a useful survey of the application of ion exchange and precipitation processes to fuel treatment and one can agree with the general inferences of the authors that they will not play a major part in nuclear fuel processing.

Part 3 treats with the non-aqueous techniques for processing irradiated fuel. These may be

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broadly classified into those processes which remove a substantial fraction of the fission products (de-poisoning) and the true separation processes, such as halogenation, liquid metal extraction and metal distillation. At one time it was considered that such processes would supplant the aqueous processes on economic grounds, especially as they could, in theory, be applied to fuels shortly after discharge from the reactor. This would greatly reduce the inventory charges of expensive fissile material in the fuel cycle. Although further study of such processes has shown then to be less attractive for thermal and fast reactor fuels, the authors rightly devote 40 pages to their description and provide an excellent account of the possible systems.

Part 4 is devoted to the disposal of radioactive effluents and the subject is introduced by a clear and concise survey of the radio-isotopes of biological significance and an estimate of the amounts of activity arising from a power programme.

A short description of the storage of highly active, fission product aqueous wastes does not give the reader an appreciation of the size of the problem nor does it describe the techniques in use in the U.K. and the U.S.A. in sufficient detail for their simplicity to be demonstrated. Again the costs in this section must be treated with reserve. The authors conclude that the storage of liquid wastes is relatively expensive, presumably when compared with the fixation techniques described in the subsequent section. This conclusion is at variance with current assessments, including one by WATSON published at the 1958 Geneva Conference.

The sections describing ground and sea disposal of medium active liquors give a well balanced picture of the techniques used in the U.K. and U.S.A. and this part of the book could be read with advantage by the intelligent layman who wishes to gain an informed view of radio-active waste disposal. The treatment of low active wastes is thoroughly described and the section devoted to the recovery of radio-isotopes such as ^{137}Cs and ^{90}Sr gives a useful survey of some of the processes which may be applied if the extraction of these fission products for industrial application ever becomes a commercial possibility.

In part 5 the authors make their own assessment of the future trends of fuel processing but wisely draw no firm conclusions; the industry is too young for its future trends to be forecast with any certainty, although a logical pattern is developing in this country which may form the basis of future nuclear power systems.

The book as a whole will form a useful addition to the library of a young graduate entering the nuclear energy industry and its bibliography should help him to search the literature efficiently.

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Vacancies and Other Point Defects in Metals and Alloys: *A Symposium.* Institute of Metals, London, 1958. 238 pp., 40s., $6.00.

A VERY large number of the properties of solid materials, such as ionic conductivity, diffusion and many mechanical and optical properties depend upon the presence of point defects in their crystalline structure. In fact, a study of these and other type defects has become in recent years almost a subject in its own right with the various physical properties merely regarded as manifestations of the presence of the defects. It was with this point of view in mind that a Symposium on the subject of "Vacancies and other point defects in metals and alloys" was held at Harwell in December 1957. The present monograph is a collection of the papers presented on that occasion, both invited and contributed in discussion.

The part played by point defects in the mechanical properties of metals and alloys at low temperatures was dealt with in a paper by A. H. COTTRELL and at high temperatures in one by D. MCLEAN. A paper by BROOM and HAM discusses the essential characteristic properties of defects and the extent to which these influence various properties such as stored energy, electrical and thermal conductivity, density, lattice constants and thermoelectric and magnetic properties. Diffusion is dealt with in a valuable review by W. M. LOMER. WILLIAMS and HAYFIELD describe the importance of point defects in oxidation and corrosion and discuss generally the influence of the surface of a solid on defect behaviour. Apparently out of place in a Symposium on metals, is a paper by P. L. PLATT on point defects and mechanical properties in ionic crystals, but defects in both materials have many properties

in common (and also some important differences) and with ionic crystals advantage can be taken of methods of study not available with metals, such as optical and ionic conductivity measurements.

The papers are generally well written and constitute very useful and detailed surveys of the state of their subjects at the time of writing. This appears to have been at least 7–8 months before the Symposium was held. More up to date are the numerous contributions to the discussion; many of these are preliminary reports of work in progress, some of which are still unpublished.

The book is a valuable addition to the literature on solid state science, is well produced, and is not unreasonably priced.

A. D. Le Claire

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THE REACTION OF ATOMIC CARBON WITH OXYGEN: SIGNIFICANCE FOR THE NATURAL RADIO-CARBON CYCLE*

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Abstract—The nuclear reaction responsible for production of natural radio-carbon in the upper atmosphere, $^{14}N(n,p)^{14}C$, can be duplicated in an atomic reactor. When ^{14}C atoms so produced are reacted with N_2–O_2 mixtures under a variety of conditions and when corrections are made for complicating radiation induced effects, ^{14}CO is found to account for 90–100 per cent of the ^{14}C produced. This result has been confirmed by work with ^{11}C in much weaker radiation fields. Previously it has been tacitly assumed that $^{14}CO_2$ must be the product of such a reaction. Since ^{14}C as CO cannot be utilized in the photosynthetic process suggested mechanisms for converting carbon monoxide into a chemical form suitable for entrance into the biosphere are reviewed. The relatively long mean life of atmospheric CO leads to the prediction that the specific activity of natural CO may quite possibly be greater than that of atmospheric CO_2, and therefore of the biosphere with which CO_2 is in equilibrium.

RADIO-CARBON is generally found in nature in the tetravalent state. It is produced by the interaction of neutrons from cosmic radiation with nitrogen in the atmosphere according to the reaction $^{14}N(n, p)^{14}C$. This ^{14}C has an energy of 40,000 eV and can thus react as a hot atom or, after collisional loss of excess energy, by thermal reaction. It has generally been tacitly assumed that the original product formed by the radio-carbon is carbon dioxide.[1] However, while it is evident that CO_2 must eventually be formed it is not at all apparent that this will be the primary reaction product. A perhaps more likely primary product is carbon monoxide which is subsequently oxidized to the tetravalent state by some unknown agency.

Possible reactions of carbon atoms with oxygen are

$$C(g) + O_2 = CO_2 \qquad \Delta H = -265{\cdot}96 \text{ kcal} \qquad (1)$$

$$C(g) + O_2 = CO + O \qquad \Delta H = -138{\cdot}96 \text{ kcal} \qquad (2)$$

CO_2 formed in reaction (1) would have an internal energy of 11·6 eV and would thus be expected only as the result of a three-body collision. Reaction (2) should therefore represent the preferred reaction in the gas phase. Part of the energy of this process will appear as kinetic energy and part as internal energy of the CO. The possibility therefore exists that the "hot" CO thus formed may undergo further reaction in its next several collisions to give CO_2 as the product of a secondary hot reaction.

Radio-carbon can be generated in a nuclear reactor by the reaction $^{14}N(n, p)^{14}C$. There is thus a method available for producing ^{14}C under conditions similar to the natural ones. We have used this method to produce ^{14}C in the presence of oxygen

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[1] E. C. ANDERSON, *Ann. Rev. Nucl. Sci.* **2**, 63 (1953).

and have investigated the products of the reaction of ^{14}C with these species under a variety of conditions. Unfortunately the environment in which ^{14}C is formed in a reactor is not exactly comparable to that in the natural situation. Radiation damage to the system due to γ-radiation accompanying the neutron flux in the reactor is much greater than in the atmosphere. However, the extent of this radiation damage can be estimated and corrections applied which compensate for its effect.

EXPERIMENTAL

The gases irradiated were air and nitrogen–oxygen mixtures, sometimes containing small amounts of CO, CO_2, and NO_2. The air was dried by pulling it through a drying tube filled with magnesium perchlorate. The other gases were obtained from The Matheson Co., Inc.: prepurified nitrogen (99·996 per cent minimum purity), extra dry oxygen (98·6 per cent minimum purity), bone dry CO_2 (99·8 per cent minimum purity), commercial grade CO (98·0 per cent minimum purity), and NO_2 (minimum purity 98·0 per cent). These gases were used without purification. Quartz tubes 5–8 cm^3 in volume were filled on a vacuum line, the total pressure being about one atmosphere.

Samples were irradiated in the Brookhaven reactor at neutron fluxes of 5×10^{12}–8×10^{13} neutrons cm^{-2} sec^{-1} for periods of 2 days and 4 hr, and at 10^{11} neutrons cm^{-2} sec^{-1} for 5, 7 and 12 days.

After irradiation a sample was placed in an opener, CO and CO_2 carrier were added if they were not present during the irradiation, and the quartz tube was crushed. Helium was flushed through the opener to inject the gas onto a chromatographic column. Most of the separations were accomplished on a silica gel column 2 ft in length. A few samples were analysed using a 5 ft silica gel or a 1 ft charcoal column. In order to separate nitrogen and oxygen from the CO it was necessary to cool the column to dry-ice temperature. After elution of the CO peak the dry-ice bath was removed and CO_2 eluted at room temperature. The gas passed from the column through a thermal conductivity cell and then through a window vapour flow proportional counter.[2] In this way the total mass of a peak as well as its activity was recorded as the peak eluted from the column.[3]

The possibility that ^{14}C activity was present as carbon or carbon suboxide polymers on the walls of the tubes was eliminated by heating the crushed quartz in the presence of CuO and O_2, with carrier CO_2 added. The resulting gas was analysed for $^{14}CO_2$. One per cent or less of the total activity was found on the walls. The fact that the observed activity in almost all experiments exceeded that calculated from the neutron dosage is a further check that no important products are unobserved.

An activity peak which is thought to be due to ^{37}A (35·0 days) from the reaction ^{36}A (n, γ) ^{37}A was found to elute with oxygen in the air samples. This substance was not oxidizable to CO_2. The amount of activity and the decay rate are consistent with what would be expected for ^{37}A. A similar activity which appears to have come from the walls of the tubes is present to a much smaller extent in the samples prepared from nitrogen and oxygen.

The mass analysis was calibrated by passing known amounts of CO through the chromatographic column and calculating the number of moles of CO that correspond to a square centimeter of peak area. From this an estimate was made of the amount of carbon monoxide oxidized in the radiation field in those experiments where carrier carbon monoxide was present.

RESULTS AND DISCUSSION

Estimation of the effect of radiation damage. Both ^{14}CO and $^{14}CO_2$ are observed in the experiments. It is known that radiation can reduce CO_2 and oxidize CO.[4,5] Therefore, since in some runs radiation energy of the order of as much as 0·5 eV/molecule is absorbed by the system care must be used in deciding what portion of the product is due to the primary reactions of the ^{14}C atoms and what portion is the result of modification by radiation processes.

Results on the N_2–O_2 systems with no added carrier are shown by the dotted line

[2] R. WOLFGANG and C. MACKAY, *Nucleonics* **16**, No. 10, 69 (1958).
[3] R. WOLFGANG and F. S. ROWLAND, *Analyt. Chem.* **30**, 903 (1958).
[4] P. HARTECK and S. DONDES, *J. Chem. Phys.* **23**, 902 (1955).
[5] P. HARTECK and S. DONDES, *J. Chem. Phys.* **26**, 1727 (1957).

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in Fig. 1. The points scatter somewhat, undoubtedly because a true carrier free run is virtually impossible and the actual amounts of impurities acting as carrier may be expected to vary from run to run. However, the rather strange double maximum does seem to be reproducible. When carrier is added (Table 1, Fig. 1) the percentage of ^{14}CO increases markedly and becomes a much less sensitive function of the N_2–O_2 composition. It appears that carrier CO tends to shield ^{14}CO from radiation oxidation. Since no activity appears on the walls of the reaction vessels ^{14}CO and

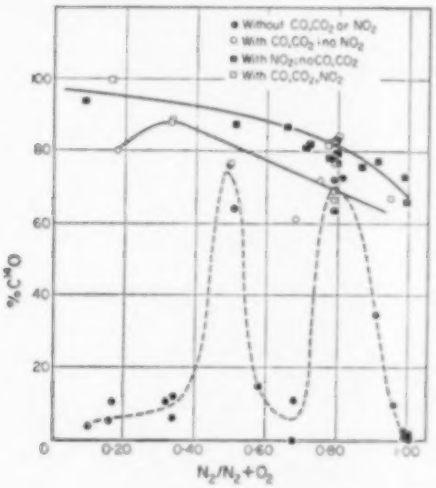

FIG. 1.—^{14}CO yield as a function of sample composition: (— ○— lower radiation field).

$^{14}CO_2$ seem to be the only products. The good agreement between the total activity found and that calculated from the neutron dosage bears out this conclusion.

In runs done with CO carrier only, the specific activity of the ^{14}CO (i.e., its total activity divided by mass of carrier present) is higher than that of the $^{14}CO_2$ showing that it must be a primary product. The amount of ^{14}CO oxidized may be estimated from the measured extent of oxidation of the carrier. This estimation of the amount of radiation oxidation gives the result that the product of the primary reaction of the ^{14}C is approximately 90 per cent or more ^{14}CO and that this is affected in only a minor way by the relative amounts of nitrogen and oxygen present. This confirms the expectation that the initial ^{14}C–O_2 collision complex is unstable, and also shows that the hot ^{14}CO produced does not undergo significant oxidation by virtue of its excess energy.*

Strong support for this conclusion derives from preliminary experiments on the reaction of hot ^{11}C (20·5 min) with N_2–O_2 mixtures. In the ^{11}C work radiation damage

* The actual mechanism of the radiation oxidation of CO in the ^{14}C system is not directly germane to the problem considered here and only a cursory attempt was made to understand it. This attempt was largely unsuccessful, as might have been anticipated from the complexity of the separate CO–CO_2 and N_2–O_2 systems as studied by HARTECK and DONDES.[6–7] It was found however that addition of extra NO_2 to the reaction mixture (beyond that produced by the radiolysis of N_2–O_2) increased the yield of ^{14}CO (Fig. 1) even in carrier free runs where the Harteck–Dondes chain radiation oxidation mechanism cannot apply. Apparently the NO_2 acts as a trap for a species capable of oxidizing CO.

is estimated as being of the order of 10^{-4} that in the ^{14}C experiments. Under these conditions 97 ± 3 per cent of the ^{11}C appears as ^{11}CO in both air and pure oxygen regardless of the presence or absence of carrier. (A more detailed account of these experiments will appear later.)

NO_2 as the possible source of ^{14}CO. There is a possibility that the ^{14}CO observed

TABLE 1.—^{14}CO YIELD UNDER VARIOUS CONDITIONS FOR SAMPLES WITH ADDITIVES

Composition of sample (%)					Neutron flux (ncm^{-2} sec^{-1})	Irradiation time (hr)	^{14}C as CO*(%)
N_2	O_2	CO	CO_2	NO_2			
96·9 air		1·6	1·5		10^{11}	293	79
97·4 air		1·2	1·2		10^{11}	293	79
97·5 air		1·3	1·2		$5·5 \times 10^{12}$	48	67
94·8 air		5·2			$6·3 \times 10^{12}$	48	69
89·9 air		3·5	6·6		10^{11}	168	77
90·7 air		3·1	6·2		10^{11}	168	83
94·5 air		2·4	3·1		$6·3 \times 10^{12}$	48	69
86·5	8·4	2·1	3·0		$8·1 \times 10^{12}$	4·2	67
70·9	23·7	2·4	3·0		$8·1 \times 10^{12}$	4·2	72
64·1	30·1	2·3	3·5		$8·1 \times 10^{12}$	4·2	61
47·4	46·7	3·5	2·4		$8·1 \times 10^{12}$	4·2	77
30·1	62·3	3·6	3·7		$8·1 \times 10^{12}$	4·2	88
16·5	78·7	2·1	2·7		$8·1 \times 10^{12}$	4·2	80
95·6 air				4·4	$5·5 \times 10^{12}$	48	79
96·1 air				3·9	$5·5 \times 10^{12}$	48	78
95·7 air				4·3	$6·3 \times 10^{12}$	48	83
94·9				5·1	$6·3 \times 10^{12}$	48	77
97·2	0·8			2·1	$6·3 \times 10^{12}$	48	66
96·2	0·8			3·0	$6·3 \times 10^{12}$	48	73
88·5	8·7			2·8	$6·3 \times 10^{12}$	48	78
85·1	13·1			1·8	$6·3 \times 10^{12}$	48	76
79·1	18·5			2·4	$6·3 \times 10^{12}$	48	81
79·1	18·5			2·4	$6·3 \times 10^{12}$	48	81
64·5	33·6			1·9	$6·3 \times 10^{12}$	48	87
49·9	48·2			1·9	$6·3 \times 10^{12}$	48	88
8·3	88·9			2·8	$6·3 \times 10^{12}$	48	94
95·5 air		0·6	0·6	3·3	10^{11}	293	83
94·4 air		1·2	1·1	3·3	10^{11}	293	82
86·9 air		9·2		3·9	$6·3 \times 10^{12}$	48	84
28·8	60·9	3·6	3·4	2·5	$8·1 \times 10^{12}$	4·2	89
14·7	75·5	2·8	3·4	3·6	$8·1 \times 10^{12}$	4·2	100

* ^{14}CO yields are not corrected for radiation oxidation. See text.

does not arise by carbon atom reaction with O_2 but rather from reaction with radiation produced NO_2.[6,7] in a manner similar to that postulated by HARTECK and DONDES to explain NO_2 inhibition of the radiation chain oxidation of CO.[4,5] *A priori* this seems unlikely since the low concentration of NO_2 present (~1 per cent or less than that of O_2) would require that the collision efficiency for reaction with NO_2 be about two orders of magnitude greater than that for O_2. Further the result that a ten-fold

[6] P. HARTECK and S. DONDES, *J. Chem. Phys.* **24**, 619 (1956).
[7] P. HARTECK and S. DONDES, *Nucleonics* **14**, No. 7, 22 (1956).

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reduction in total radiation dose causes but a minor change in the yield of $^{14}CO_2$ is not obviously consistent with such an hypothesis. (This change in $^{14}CO_2$ yield is probably caused by the reduction in the concentration of NO_2 which is acting as an inhibitor for the oxidation of $^{14}CO^*$.) However, the best proof that C will react with O_2 to give CO is again the ^{11}C work where radiation damage and hence NO_2 concentration appear to be negligible.

The pathway of natural radio-carbon. If natural radio-carbon is introduced into the earth's atmosphere as CO there remains the problem of how it reaches the tetravalent state either as CO_2 or in the biosphere. Although radiation oxidation of CO in air proceeds with G values of the order of 10 or 12[8,9] the relatively low radiation flux in the atmosphere rules this out as a direct means of oxidation of atmospheric ^{14}CO. Other possible processes have been thoroughly reviewed by BATES[10,11] whose conclusions we cite. From the concentration of CO and estimates of its rate of production by combustion and from other sources he estimates the average life of a CO molecule to be less than four years. Compared to this the half time for oxidation by O, OH or HO_2 produced by photo-dissociation in the upper atmosphere appears to be very long. Oxidation of CO by O_2 has been shown to be negligible and the reactions with NO_2 and O_3 have too high an activation energy to be important. Thus, BATES argues, some other process must account for the disappearance of CO. A mechanism does exist for the biological oxidation of CO at the surface of the earth. CO confined to the earth disappears much more rapidly than expected from simple diffusion. The organism responsible for this appears to be B. oligocarbophilus, which is present in the soil.[12] This bacterium can be cultivated on inorganic media in an atmosphere of CO and air containing no other source of carbon. We are led to the interesting conjecture that natural radio-carbon, initially produced as CO, probably passes through B. oligocarbophilus in order to enter the normal biosphere.

It is instructive to calculate the specific activity of naturally radio-active carbon monoxide. Given that ^{14}C has a decay constant of λ years^{-1}, and that the mean life with respect to oxidation of an atmospheric ^{14}CO molecule is τ years, then the probability that the ^{14}C will decay while it is in the form of ^{14}CO is $(1 - e^{-\lambda\tau})$ which is well approximated by $\lambda\tau$ since $\lambda\tau$ is small. Now if the rate of production, which is equal to the rate of disintegration of ^{14}C, is $\bar{Q}$ atoms/sec cm^2 of earth's surface† and if b is the number of grammes of C as CO per square centimetre of earth's surface, the natural specific activity of CO, S, is given by

$$S = \frac{\lambda\tau\bar{Q}}{b} \text{ disintegrations/sec g C}$$

For λ use 0·693/5700 years^{-1}, and for $\bar{Q}$ use 2·6 atoms/cm^2 sec. Then $S = 3{\cdot}2 \times 10^{-4}$

† This tacitly assumes that ^{14}C once oxidized to CO_2 will not re-enter the atmosphere as CO. An equivalent assumption is that the mass of CO produced on earth originates from "dead" or inactive carbon. This follows the conclusion of BATES that its main source is combustion of motor fuels. If this assumption is incorrect a term of up to 16 disintegrations/min/gC, the natural activity of CO_2, must be added to the specific activity, S, of CO calculated above.

[8] C. ROSENBLUM, *J. Amer. Chem. Soc.* **55**, 220 (1933).
[9] S. C. LIND and C. ROSENBLUM, *Proc. Nat. Acad. Sci., Wash.* **18**, 374 (1932).
[10] D. R. BATES, *The Earth as a Planet* (Edited by G. P. KUIPER) p. 592. University of Chicago Press (1954).
[11] D. R. BATES and A. E. WITHERSPOON, *Mon. Not. R. Astr. Soc.* **112**, 101 (1952).
[12] S. A. WAKSMAN, *Principles of Soil Microbiology* (2nd Ed.), p. 98. Bailliere, Tindall and Cox, London (1931).

τ/b disintegrations/sec g C. Values for b vary.[13,14] Using HUTCHINSON's best average value,[13] $5{\cdot}4 \times 10^{-5}$ g C/cm^2, $S = 5{\cdot}9\,\tau$ disintegrations/sec g C or $350\,\tau$ disintegrations/min g C. Compared with the normal natural specific activity of biospheric carbon, 16 disintegration/min g C as CO_2, this is a high specific activity even if the mean life of CO, τ, is as small as 0·1 years. However, the value of the amount of atmospheric CO, b, is as noted above quite uncertain. It is hoped that measurements of the specific activity of carbon monoxide will shed some light on both the CO inventory and the mean life of a CO molecule in nature, that is on b and τ. If natural carbon monoxide is indeed found to be more radioactive than natural carbon dioxide we will have the further consequence that B. oligocarbophilus is probably the naturally "hottest" organism on earth in terms of ^{14}C specific activity.

[13] G. E. HUTCHINSON, *The Earth as a Planet* (Edited by G. P. KUIPER) p. 393. University of Chicago Press (1954).
[14] L. GOLDBERG, *The Earth as a Planet* (Edited by G. P. KUIPER) p. 478. University of Chicago Press (1954).

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THE DIPOLE MOMENT OF OF_2

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A contribution from the Department of Chemistry of the Agricultural and Mechanical College of Texas

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Abstract—The dipole moment of OF_2 has been determined from the Stark effect on two rotational frequencies. The dipole moment of 0·1759 ± 0·0010 Debye is about 2·1 per cent of that calculated for a simple ionic model.

RECENTLY, the structure of OF_2 has been determined by HILTON[1] using microwave spectroscopy techniques. The determination of the dipole moment seemed to be indicated as an additional study.

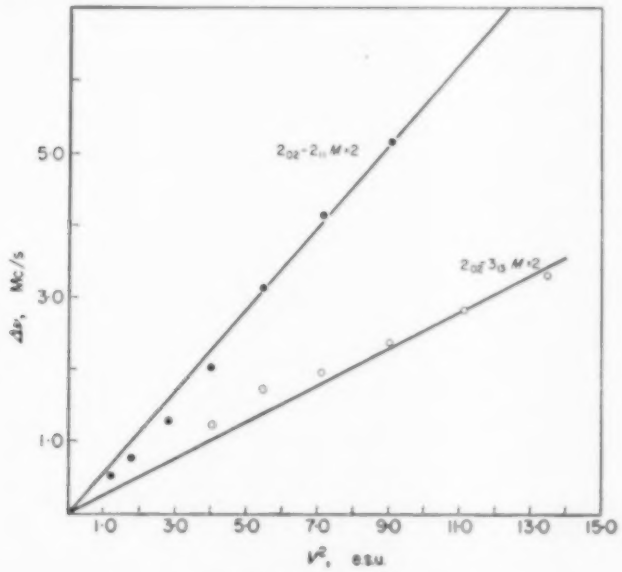

FIG. 1.—Stark effect for OF_2.

EXPERIMENTAL

The Stark effect was observed using a conventional Stark spectrometer modulated at 4 kc/s. The cell was calibrated using the shift of the 3 ⟶ 4 transition of OCS as a standard. Fig. 1 shows the observed Stark shifts for OF_2 as a function of field. Measurements were made only on the stronger and sharper Stark components. The method of GOLDEN and WILSON[2] which employs the line strength elements tabulated by CROSS *et al.*[3] and extended by SCHWENDEMAN and LAURIE[4] was

[1] A. R. HILTON, Ph.D. Dissertation, A and M College of Texas (1959).
[2] S. GOLDEN and E. B. WILSON, JR., *J. Chem. Phys.* **16**, 669 (1948).
[3] P. C. CROSS, R. M. HAINER and G. W. KING, *J. Chem. Phys.* **12**, 210 (1944).
[4] R. H. SCHWENDEMAN and V. W. LAURIE, *Tables of Line Strengths*. Pergamon Press, London, New York (1959).

used for the calculations. The value of k (Ray's asymmetry parameter) is -0.92961.[1] The results from the $2_{02} \longrightarrow 2_{11}$ transition indicate a dipole moment of 0·1753 Debye while those from the $2_{02} \longrightarrow 3_{12}$ transition indicate a dipole moment of 0·1766 Debye. An average value of 0·1759 $\pm$ 0·0010 Debye seems reasonable.

DISCUSSION

The results of HILTON indicate that the bond angle, 2θ for OF_2 is 103·88° while the O—F bond distance is 1·385 Å. If one considers a molecule with the structure $O^{2+}(F^-)_2$ in which the charges are centred on the nuclear positions, we can calculate a dipole moment for it in the following manner. The moment along the O—F bond would be the product of the electronic charge times the bond length. The component along the symmetry axis would be this value times $\cos\theta$. Since there are two such components, the dipole moment would be twice this value. The dipole moment calculated in this way is 8·2 Debye units. The observed dipole moment for OF_2 is a very small part, about 2·1 per cent of that calculated for the simple ionic model considered here.

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THE ABSORPTION SPECTRA OF COMPLEX SALTS—III
CUPRIC ETHYLACETOACETATE*

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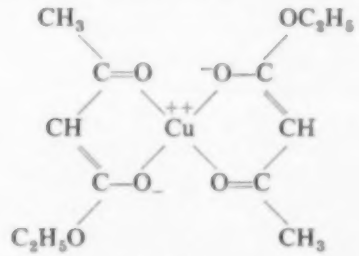
(*Received* 30 *September* 1959)

Abstract—The absorption spectra of cupric ethylacetoacetate in the 200–1000 mμ range have been measured in a variety of solvents. Absorption bands of high intensity in the 200–300 mμ region are attributed to the conjugated system of the ligand. Absorption in the 300–1000 mμ region is shown to be resolvable into three Gaussian component bands at wavelengths of approximately 370 mμ, 550 mμ and 700 mμ in non-reacting solvents and 370 mμ, 700 mμ and 900 mμ in heterocyclic bases, which react with the solute. Correlations are suggested between these absorption bands and possible $d \rightarrow d$ transitions in the cupric ion.

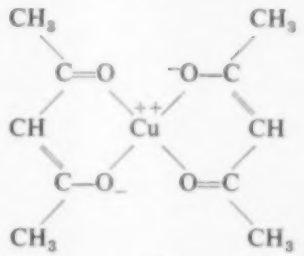
ALTHOUGH the apparent co-ordination number of the cupric ion in hydrated and complex salts is commonly four, an elongated octahedral environment is usually achieved in the solid state by further co-ordination of donor atoms along the axis normal to the plane of 4:co-ordination.[1] A parallel situation probably arises in aqueous solutions by the analogous co-ordination of solvent molecules. The absorption spectra of aqueous solutions are thus characterised by a single absorption band corresponding to the $d_\varepsilon \rightarrow d_\gamma$ transition expected for a d^9 ion in an octahedral ligand field;[2] this band has its maximum intensity in the region 550–800 mμ depending on the nature of the ligands, there being no absorption in the near ultra-violet region.

There are, however, some 4:co-ordinated cupric complexes which are soluble, monomeric non-electrolytes in non-donor solvents and so must retain their planar structure in solution without enlargement of the co-ordination number to six. In these compounds the tetragonal environment of the cupric ion should lead to a more complex splitting of the *d*-orbital energy levels and so to more complex absorption spectra. Compounds of this type are formed mainly by the enolate ions of β-diketones and related substances, such as acetylacetone, ethyl acetoacetate and salicylaldehyde.

In the present work the absorption spectra of cupric ethylacetoacetate (I) have



(I)



(II)

* Part II: *J. Inorg. Nucl. Chem.* **7**, 73 (1958).

[1] A. F. WELLS, *Structural Inorganic Chemistry* (2nd Ed.). Oxford University Press (1950).
[2] J. S. GRIFFITH and L. E. ORGEL, *Quart. Rev.* **11**, 381 (1957).

been determined in a variety of solvents. In general there are three regions of absorption in the 200–1000 mμ region, viz.

(1) Absorption bands of high intensity in the ultra-violet region at a frequency of 3–5 μ^{-1} (330–200 mμ). In cyclohexane solution these bands show fine structure, but this is damped in more polar solvents (Fig. 1). Cupric acetylacetonate (II) shows similar absorption in the ultra-violet region, a little more intense and at a slightly lower frequency, and as the enolate ion of acetylacetone in aqueous solution also

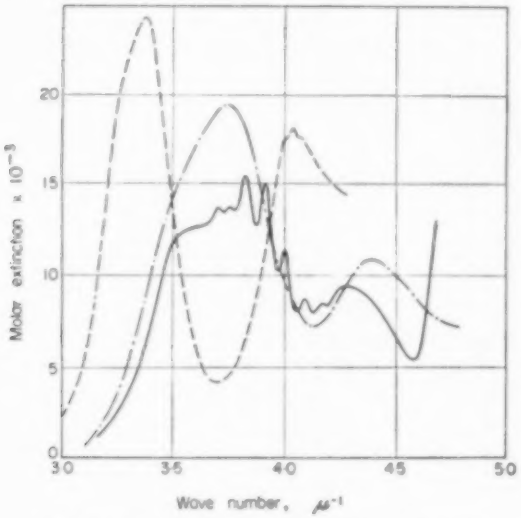


FIG. 1.—High intensity ultra-violet absorption spectra of
——— cupric ethylacetoacetate in cyclohexane,
—·— cupric ethylacetoacetate in diethyl ether,
– – – – cupric acetylacetonate in chloroform.

absorbs in this region at a slightly lower frequency than that of ethyl acetoacetate,[3] the absorption of the cupric complexes in this region may reasonably be attributed to the conjugated system of the ligand.

(2) An absorption band of intermediate intensity ($\varepsilon \sim 300$) in the near ultra-violet at a frequency of about 2·7 μ^{-1} (370 mμ) appearing as a shoulder on the low-frequency side of the high-intensity band (Fig. 3). This band also occurs, at about the same frequency, in the absorption spectra of the acetylacetonate, but is there more heavily obscured by the tail of the high-intensity band. The absorption in this region can be resolved into a single Gaussian absorption band with maximum intensity at a frequency of about 2·7 μ^{-1} and a residual absorption due to the tail of the high-intensity band (Fig. 2).

Table 1 gives the parameters of the Gaussian absorption bands obtained by carrying out this resolution in seven different solvents. In most of these the shoulder of the absorption curve is sufficiently well defined for the resolution to be reasonably accurate, but in cyclohexane solution the band in the near ultra-violet is so deeply embedded in the high-intensity absorption that the analysis can only be approximate.

[3] A. E. GILLAM and E. S. STERN, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*. Arnold, London (1954).

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(3) In the visible region there are overlapping absorption bands of low intensity ($\varepsilon < 100$), responding in different ways to changes of solvent. With increasing basicity of the solvent the extinction increases at frequencies below about 1·7 μ^{-1} and decreases at higher frequencies (Fig. 3). The effects of pyridine and piperidine are very much greater than those of other solvents, and as heterocyclic bases have

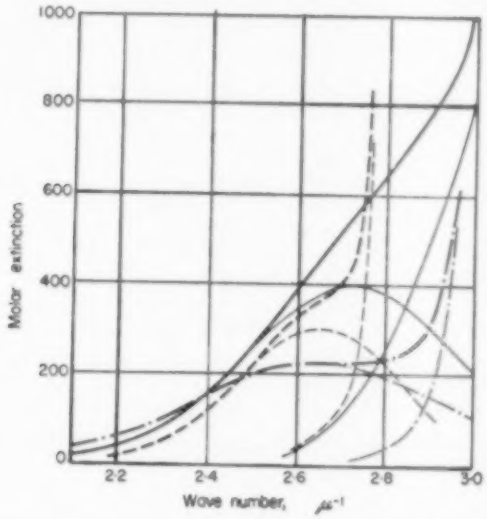

FIG. 2.—Gaussian analysis of absorption in the near ultra-violet. Heavy lines show the experimental absorption curve, light lines the constituents.
——— cupric ethylacetoacetate in cyclohexane,
—·— cupric ethylacetoacetate in pyridine,
– – – – cupric acetylacetonate in chloroform.

TABLE 1.—GAUSSIAN ABSORPTION BANDS IN THE 2·7 μ^{-1} REGION

Solvent	ν_{max} (μ^{-1})	ϵ_{max}	Width (μ^{-1})
Cyclohexane	2·72	400	0·55
Benzene	2·66	290	0·61
CCl_4	2·70	280	0·60
Ether	2·73	360	0·60
Acetone	2·70	270	0·60
Pyridine	2·64	220	0·64
Piperidine	2·63	180	0·55

been shown to combine with the solute,[4] experiments were carried out to determine whether such reactions occurred with the other solvents.

Fig. 4 shows the extinction, at arbitrarily chosen frequencies, plotted against the solvent composition for mixtures of cyclohexane with some of the other solvents. The linear plots obtained with benzene, ether and acetone show that there is no reaction between these solvents and the solute, whereas pyridine and piperidine give

[4] D. P. GRADDON, *Nature, Lond.* **183**, 1610 (1959).

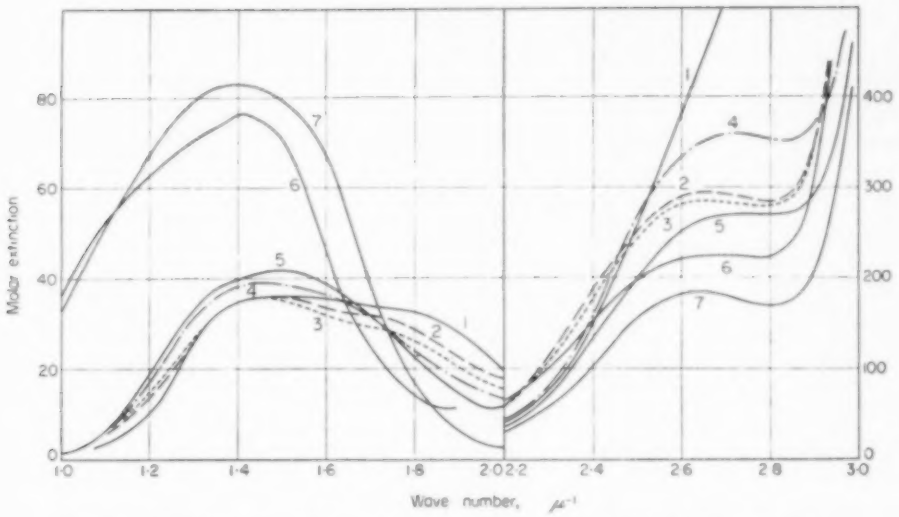

FIG. 3.—Absorption spectra of cupric ethylacetoacetate in the visible and near ultra-violet regions in seven different solvents: cyclohexane (1), benzene (2), carbon tetrachloride (3), diethyl ether (4), acetone (5), pyridine (6) and piperidine (7).

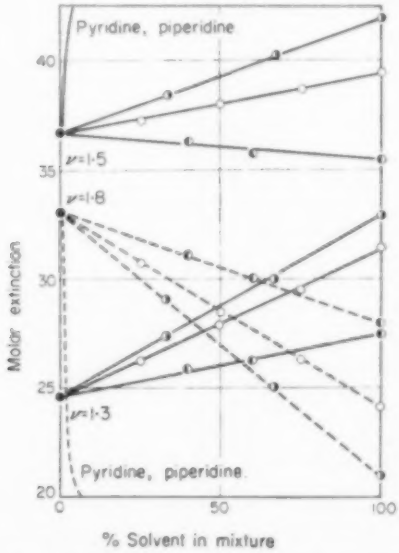

FIG. 4.—Extinction of solutions of cupric ethylacetoacetate in mixtures of cyclohexane with benzene ◐, diethyl ether ○, and acetone ◑. Part of the curves are shown for the extinction in mixtures containing pyridine or piperidine.

curved plots indicative of compound formation. The absorption spectra in pyridine or piperidine as solvent thus represent a different absorbing species from those in the other solvents and may be expected to differ fundamentally from the absorption spectra in these solvents.

In each case absorption in the visible region can be resolved into two Gaussian

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components. In the non-combining solvents these have maximum intensities at frequencies of about 1·4 μ^{-1} (700 mμ) and 1·8 μ^{-1} (550 mμ) and in pyridine and piperidine at about 1·1 μ^{-1} (900 mμ) and 1·4 μ^{-1} (700 mμ) (Figs. 5–6). The parameters of the component Gaussian absorption bands are given in Table 2.

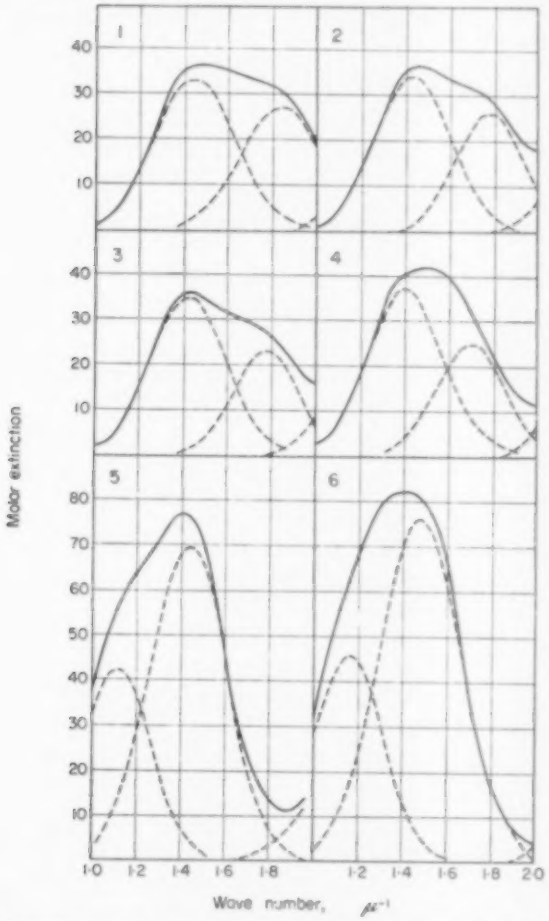

FIG. 5.—Gaussian analysis of the visible region absorption of solutions of cupric ethylacetoacetate in cyclohexane (1), benzene (2), carbon tetrachloride (3), acetone (4), pyridine (5) and piperidine (6).

These results may be compared with those obtained by CALVIN *et al.* for the absorption of cupric acetylacetonate in a similar range of solvents.[5] Their experimental results, which are restricted to the visible region, parallel exactly those now reported for cupric ethylacetoacetate and extension of their observations to the ultra-violet region shows that cupric acetylacetonate also produces an absorption band of intermediate intensity at a frequency of about 2·7 μ^{-1} (Fig. 2) and high intensity bands at higher frequencies (Fig. 1), though these obscure the intermediate band more severely than in the ethylacetoacetate.

[5] R. C. BELFORD, M. CALVIN and G. BELFORD, *J. Chem. Phys.* **26**, 1165 (1957).

In interpreting their results, however, these authors resolved the absorption in the visible region into three Gaussian component bands in each case instead of two. Unfortunately, as they point out, these component bands overlap to such an extent that it is not possible to make a unique analysis and, as can be seen in Fig. 6, it is in fact possible to represent the experimental curves equally satisfactorily as the sum of either two or three Gaussian components.

TABLE 2.—GAUSSIAN ABSORPTION BANDS IN THE VISIBLE REGION

Solvent	ν_{max} (μ^{-1})	ϵ_{max}	Width (μ^{-1})	ν_{max} (μ^{-1})	ϵ_{max}	Width (μ^{-1})
Cyclohexane	1·45	33	0·42	1·84	27	0·42
Benzene	1·43	34	0·40	1·78	26	0·36
CCl_4	1·43	35	0·40	1·78	23	0·34
Ether	1·40	35	0·40	1·71	23	0·36
Acetone	1·40	37	0·40	1·70	25	0·36
Pyridine	1·44	70	0·40	1·12	43	0·36
Piperidine	1·48	76	0·44	1·16	46	0·36

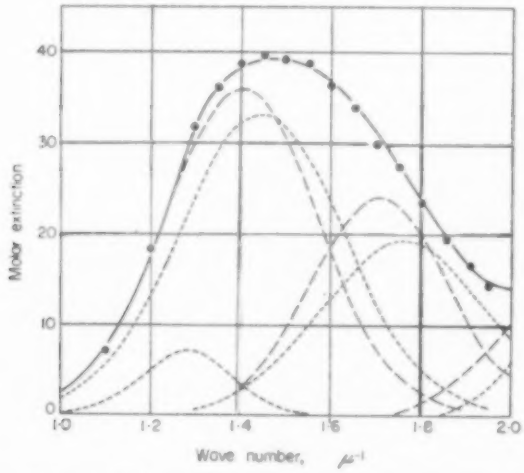

FIG. 6.—Gaussian analysis of the absorption of cupric ethylacetoacetate in diethyl ether into two (— — —) or three (– – –) absorption curves. Ringed points show the sum of the two (⊗) or three (⊕) curves.

In the present work, resolution into two components is preferred for several reasons:

(1) A more regular variation is observed in the parameters of the component bands on changing from one solvent to another (Table 2).

(2) The visible region absorption of cupric ethylacetoacetate in cyclohexane and of the acetylacetonate in chloroform cannot be resolved into three components. CALVIN *et al.* attempted to account for the missing band in their analysis by calculating that its frequency should be nearly the same as that of one of the other bands; they

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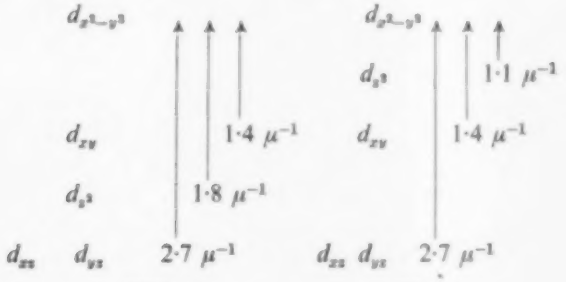
admit however that their calculation is open to doubt, and the frequency proposed is not wholly consistent with the position of the missing band which would be expected from a study of their tables.

(3) By resolving all of these curves into three components the absorption in pyridine and piperidine is made to conform to the pattern set by the other solvents; but it is now shown that pyridine and piperidine react with the solutes to form new species, the absorption of which ought not to conform to the pattern in the other solvents.

Since ligand-field theory predicts a fourfold splitting of the *d*-orbital energy levels in a tetragonal field, we should expect to find three $d \rightarrow d$ transition energies represented by three absorption bands.[6] BELFORD *et al.* identify these with their three Gaussian components of the absorption in the visible region, but as they are apparently unaware of the absorption band in the near ultra-violet (2·7 μ^{-1}), this band remains unidentified in their analysis. On the basis of resolution of the visible region absorption into two components only, and allowing for the band in the near ultra-violet, it is now possible to express the absorption of cupric ethylacetoacetate (or the acetylacetonate) in terms of three Gaussian components, one of which is shifted to much lower frequency on the formation of a new species in pyridine or piperidine solution. The approximate frequencies of these three components are:

in non-reacting solvents:	1·4	1·8	2·7 μ^{-1}
in pyridine or piperidine:	1·4	1·1	2·7 μ^{-1}

Correlation of these bands with particular electronic transitions is, at best, a largely intuitive process, since it is not possible to calculate even the order of increasing energy of the *d*-orbitals, except in an idealised environment of the metal atom. However, the high sensitivity of the absorption band at 1·8 μ^{-1} to changes of solvent and its replacement by a band at 1·1 μ^{-1} when a molecule of pyridine or piperidine is added to the compound, presumably by co-ordination along the axis normal to the molecular plane, suggests that both of these bands should be attributed to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, since the energy of the d_{z^2} orbital will certainly be considerably raised by co-ordination of further ligands in this manner. On the assumption that the d_{xy} orbital, which lies in the molecular plane, is of higher energy than the doubly degenerate d_{xz} and d_{yz} orbitals, we thus arrive at the tentative assignments of energy levels and electronic transitions shown in III and IV.



[6] L. E. ORGEL, *J. Chem. Phys.* **23**, 1004 (1955).

Symmetry forbidden $d \rightarrow d$ transitions of this type are made possible by vibrational perturbations, the nature and effects of which are discussed in some detail by CHATT *et al.* in their analysis of the absorption spectra of some platinous ammines.[7] They show in particular that the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition is probably associated with the absorption of light polarized in the z axis. The polarization of the absorption of cupric complexes of the type here discussed is not known, but it is significant that cupric acetate, in which the cupric ion also has a planar environment, also has an absorption band in the near ultra-violet at a frequency of about 2·7 μ^{-1}, shown by TSUCHIDA and YAMADA to be polarized in the z axis.[8] TSUCHIDA and YAMADA attribute this absorption band to the "Cu–Cu linkage" in the dimeric acetate, but as an absorption band at this frequency appears in the spectra of the acetylacetonate and related compounds, it seems more probable that it is characteristic of the planar co-ordinated cupric ion that of the "Cu–Cu linkage" peculiar to the alkanoates, and that in both types of compound it represents the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition.

In the cupric alkanoates the extinction of this band is of the order of 50–70, as is common with $d \rightarrow d$ singlet transitions, but in the enolates here discussed it is much higher, reaching a maximum of about 400 in cyclohexane solution. This high extinction appears to be due to some form of interaction with the high-intensity absorption, and is observed in other instances where a $d \rightarrow d$ absorption band is embedded in the tail of a band of high intensity (for example an extinction of 233 is quoted for the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition in the $[(NH_3)_3PtCl]^+$ ion by CHATT *et al. loc. cit.*)

EXPERIMENTAL

Cupric ethylacetoacetate was prepared by reaction of cupric sulphate with the equivalent quantities of ethylacetoacetate and sodium hydroxide in aqueous solution. The green precipitate thus obtained was dried over sulphuric acid *in vacuo* and recristallized twice from benzene as dull green needles (Found: Cu (iodimetric), 19·7. Calc. for $Cu(CH_3CO.CH.CO_2C_2H_5)_2$: 19·77%).

Cupric acetylacetonate was prepared in a similar manner and recrystallized from glacial acetic acid as steely blue needles. (Found: Cu (iodimetric), 24·3. Calc. for $Cu(CH_3CO.CH.COCH_3)_2$: 24·30%).

Solvents were analytical reagent grade, purified by redistillation and dried (ether and acetone) over anhydrous sodium sulphate. Pyridine was heated under reflux with potassium permanganate before distillation.

Absorption spectra were determined on a Unicam SP500 spectrophotometer. In the visible region concentrations of 5×10^{-3} molar were used in cells of 1 cm path; in the ultra-violet region concentrations of 5×10^{-4} molar were used in conjunction with cells of 1 cm path in the range 500–330 mμ and 0·2 cm. path at shorter wavelengths.

[7] J. CHATT, G. A. GAMLEN and L. E. ORGEL, *J. Chem. Soc.* 486 (1958).
[8] R. TSUCHIDA and S. YAMADA, *Nature, Lond.* **176**, 1171 (1955).

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J. Inorg. Nucl. Chem., 1960. Vol. 14, pp. 169 to 178. Pergamon Press Ltd. Printed in Northern Ireland

INFLUENCE OF FLUORINE SUBSTITUTION ON THE PROPERTIES OF METAL CHELATE COMPOUNDS—III

URANYL(VI) CHELATE COMPOUNDS*

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Abstract—Ultra-violet, visible and infra-red absorption spectra of uranyl chelates of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone are described and interpreted on the basis of the electronic influences of the fluorine atoms. Infra-red assignments are made in the carbonyl region. Factors involved in the preparation of uranyl chelates are discussed.

IN the previous two articles of this series[1,2] the copper(II) chelates of a series of bidentate ligands,[1] and of a series of Schiff bases derived from diamines and the same bidentate ligands, have been described, and the influence on the spectra resulting from fluorine substitution on the ligand has been reported. In the present paper the influence of fluorine in the ligand on the spectra of a number of analogous uranyl chelates is described. One of the purposes of this work was to investigate the possibility of preparing uranyl chelates with properties which would allow their use in liquid scintillation counters. For this purpose, the chelates should be soluble in hydrocarbon solvents and pass a maximum of blue light in such solutions. Thus most uranyl chelates, which are coloured deep yellow or orange, are unsuitable since they would absorb the blue scintillations. It was hoped that fluorine-containing ligands would produce uranyl chelates with better properties in this respect.

Although the uranyl chelates of acetylacetone and trifluoroacetone have been known for a long time,[3] there has been no investigation of the spectra of the fluorinated derivatives of uranyl acetylacetonate until the report by HASZELDINE *et al.*[4] of the ultra-violet spectrum of bistrifluoroacetylacetono-UO_2(VI). At the writing of the present article, no reports of the preparation or spectra of the hexafluoroacetylacetone uranyl chelate have appeared.

EXPERIMENTAL

The ligands used in this investigation either were readily obtainable as pure materials, or were prepared as described in previous publications on the synthesis of the corresponding copper chelates.[1,2] The absorption spectra were measured by methods described in a previous publication.[1]

Bisacetylacetono-UO_2(VI). To 4·24 g (0·010 mole) of uranyl acetate disolved in 100 ml of water was added 2·0 g (0·020 mole) of acetylacetone dissolved in a minimum amount of warm water. An equivalent amount of aqueous K_2CO_3 solution was then added very gradually so as not to cause precipitation of uranyl hydrolytic products. The yellow-orange substance which slowly crystallized out of the orange reaction mixture was recrystallized from a toluene–petroleum ether solvent. The

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‡ National Science Foundation Fellow, 1953–4 and 1954–5.
§ On leave during summer of 1953 from Clark University, Worcester, Massachusetts.
[1] R. L. BELFORD, A. E. MARTELL and M. CALVIN, *J. Inorg. Nucl. Chem.* **2**, 11 (1956).
[2] A. E. MARTELL, R. L. BELFORD and M. CALVIN, *J. Inorg. Nucl. Chem.* **5**, 170 (1958).
[3] W. BILTZ and J. A. CLINCH, *Z. Anorg. Chem.* **40**, 220 (1904).
[4] R. N. HASZELDINE, W. K. MUSGRAVE, F. SMITH and L. M. THURTON, *J. Chem. Soc.* 609 (1951).

product, consisting of 2·5 g (53 per cent of the theoretical amount) of fine yellow needles, did not melt under 300°C, but gradually darkened as the temperature was raised. (Found: C, 25·44; H, 3·4; U, 48·0. Calc. for $C_{10}H_{14}O_8U$: C, 25·65; H, 3·0%; U, 50·9. Calc. for $C_{10}H_{14}O_8UH_2O$: C, 24·68; H, 3·32; U, 49·0).

Bistrifluoroacetylacetono-UO_2(VI). A solution of 4·24 g (0·010 mole) of uranyl acetate in 100 ml of hot water was added to a partial suspension of 3·08 g (0·020 mole) of trifluoroacetylacetone in 150 ml of boiling water. A yellow solid began to crystallize immediately. After the reaction mixture was allowed to cool, 5.0 g (87 per cent of the theoretical amount) of crystalline material was obtained. It was recrystallized by evaporation of its solution in a chloroform–carbon tetrachloride mixture. Material remaining in the mother liquor was recovered by the addition of petroleum ether. The yellow crystals thus obtained decomposed when heated above 160°. (Found: C, 20·4; H, 2·2; U, 40·2. Calc. for $C_{10}H_8O_8F_6U$: C, 20·8; H, 1·4; U, 41·3%. Calc. for $C_{10}H_{10}O_7F_6U$: C, 20·2; H, 1·7; U, 40·0).

Bishexafluoroacetylacetono-UO_2(VI) tetrahydrate. A solution of 3·40 g (0·010 mole) of uranyl chloride, UO_2Cl_2, and approximately 5 g (0·024 mole) of hexafluoroacetylacetone in 100 ml of anhydrous ether was heated for 1 hr near the boiling point. After addition of 0·8 g of NaOH and 20 min further heating, the solution which contained a finely-divided insoluble material was washed with two 100 ml portions of water. The ether solution was evaporated to near dryness and the residue was dissolved in boiling petroleum ether (30–60°). The yellow crystals obtained on cooling were twice recrystallized from petroleum ether to give a yield of 5·2 g or 76 per cent of the theoretical amount. (Found: U, 31·5, 31·9. Calc. for $C_{10}H_2O_6F_{12}U$: U, 34·8. Calc. for $C_{10}H_2O_6F_{12}U.4H_2O$: U, 31·5%).

The product was found to be insoluble in water but soluble in all organic solvents tried. The solubility in n-heptane was measured as 0·50 g in 100 ml of solvent. When heated above 58° this material changes to a substance insoluble in petroleum ether and loses a volatile liquid. It turns orange at 152° and melts with decomposition at 158–161°. The orange-red compound is also formed at 0·01 mm Hg pressure at 60° for 6 hr, and very rapidly changes to the yellow, soluble variety on exposure to air.

Reaction of bisacetylacetoneethylenediimine with the uranyl(VI) *ion.* A 0·011 mole (2·50 g) sample of ligand was dissolved in 150 ml of water at 40° and treated with 0·010 mole (4·24 g) of uranyl acetate dissolved in 200 ml of water at 40°. Turbidity gradually appeared as the temperature was raised to 60°, and then increased very rapidly as 1·0 g (0·010 mole) of sodium carbonate was slowly added with stirring. The bright yellow-orange solid, which weighed 4·2 g, was found to be soluble in dioxane, chloroform, hot toluene, and to precipitate slowly when ligroin was added to the corresponding solutions. It was recrystallized by evaporation of a chloroform solution, addition of carbon tetrachloride, and further evaporation. Further recrystallization was carried out from hot toluene by the addition of an equivalent amount of ligroin.

The same product was obtained by a different procedure whereby the uranyl acetate was first converted to the acetylacetonate,which was then treated in 25 per cent ethanol at 75° with the equivalent amount of ethylenediamine. The yellow chelate compound was completely precipitated after 15 min heating at 80°.

Repeated crystallizations from various combinations of solvents including chloroform, carbon tetrachloride and petroleum ether gave materials of slightly-varying composition, as is indicated by the following sample analyses:

Sample No.	C(%)	H(%)	N(%)
1	33·2	3·8	2·6
2	34·6	4·2	2·4
3	33·8	3·9	2·6
4	32·4	4·4	2·4
5	32·3	4·2	2·5

Reaction of bisacetylacetonetrimethylenediimine with uranyl(VI) *ion.* The procedure described above for the reaction of uranyl ion with bisacetylacetoneethylenediimine was followed exactly with

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bisacetylacetonetrimethylenediimine. The analogous substance thus obtained was recrystallized gradually from a carbon tetrachloride solution by the addition of petroleum ether. The product consisted of beautiful orange-yellow needles. (Found: C, 31·3; H, 4·1; N, 2·4%).

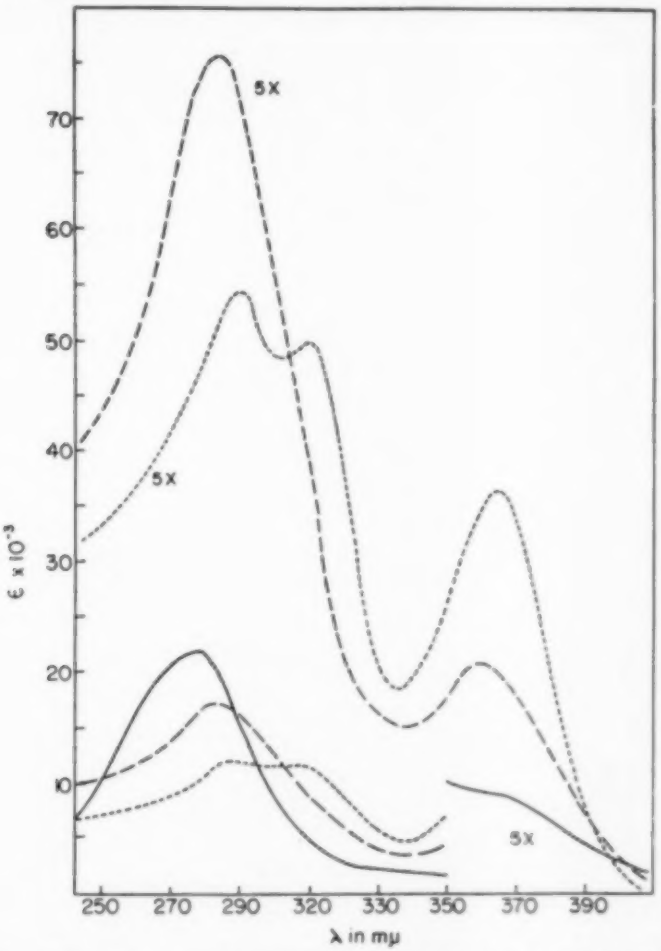

FIG. 1.—Ultra-violet absorption spectra of bisacetylacetono–UO_2(VI) ——, bistrifluoroacetylacetono–UO_2(VI) — — —, and bishexafluoroacetylacetono–UO_2(VI) – – –, in 0·000020 M and 0·0001 M chloroform solution. For the 0·0001 M solutions, 5×10^{-3} ϵ is plotted; for the 0·000020 M, $10^{-3}\epsilon$.

EXPERIMENTAL RESULTS

The ultra-violet and visible absorption spectra of the three uranyl chelates described above are given in Figs. 1 and 2, respectively.* Enlarged curves of the more interesting portions of the visible spectra are given in Fig. 3. Through the use of a semi-log scale, the ordinates of the absorption plots are made to read directly in extinction coefficient. The wavelengths of the maxima in the absorption bands in the visible and

* One cannot say that the small apparent discrepancies between spectra of the same compound in Fig. 1 are real, as the spectrophotometer used (Beckman Model DK) was not operating at peak efficiency; nor can it be very reliable at the high optical densities represented by the left-most sections of the upper curves

ultra-violet regions, with the corresponding molar extinction coefficients, are given in Table 1. Subsidiary bands, adjacent to, and partly obscured by, a primary band, are indicated in parentheses.

The infra-red spectra of the chelates and of the corresponding ligands are given in

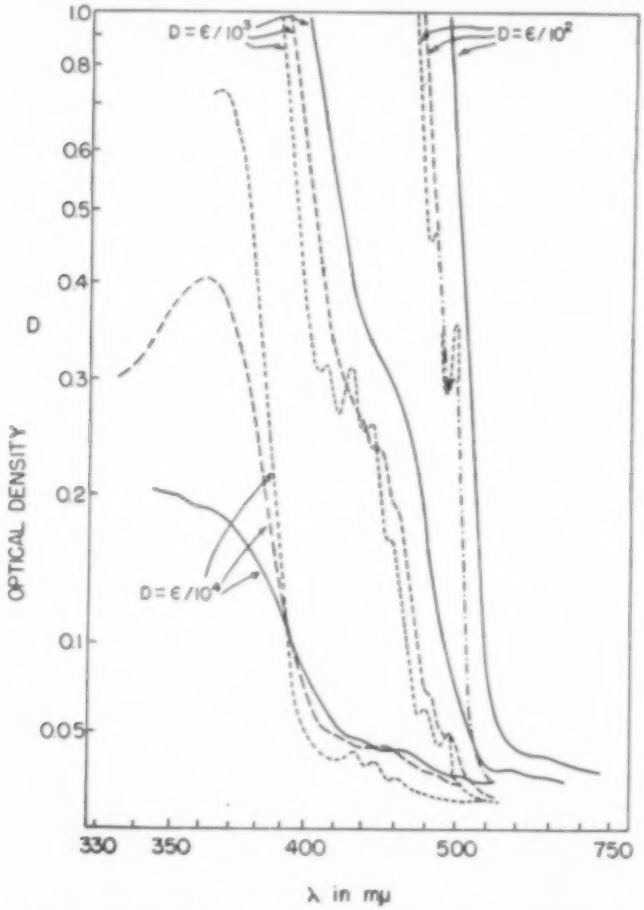

FIG. 2.—Visible and ultraviolet absorption spectra of bisacetylacetono uranyl(VI) ——, bistrifluoroacetono uranyl(VI) — — —, and bishexafluoroacetylacetono uranyl(VI) - - -, $1{\cdot}0 \times 10^{-4}$, $1{\cdot}0 \times 10^{-3}$ and $1{\cdot}0 \times 10^{-2}$ M in chloroform solution.

Table 2. The absorption frequencies of very weak or doubtful infra-red bands are also enclosed in parentheses.

DISCUSSION

Preparation of uranyl(VI) *chelate compounds.* The method outlined for the preparation of uranyl acetylacetonate and its trifluoro derivative is dependent on the rate of addition of base. Too rapid an increase in pH of the reaction mixture results in side reactions leading to the formation of hydrolytic products of the UO_2^{2+} ion, and consequent contamination of the metal chelate which is formed at the same time.

The dihydrate of hexafluoroacetylacetone was found to be relatively inactive

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toward the uranyl ion in aqueous solution. Hence it was found necessary to form the chelate from the anhydrous ligand in a non-aqueous system. One of the methods employed—involving the ligand itself as solvent and dehydrating agent—gives excellent yields. However, any similar method with a suitable non-protonic organic solvent was found to work just as well. The observed non-reactivity of the uranyl ion

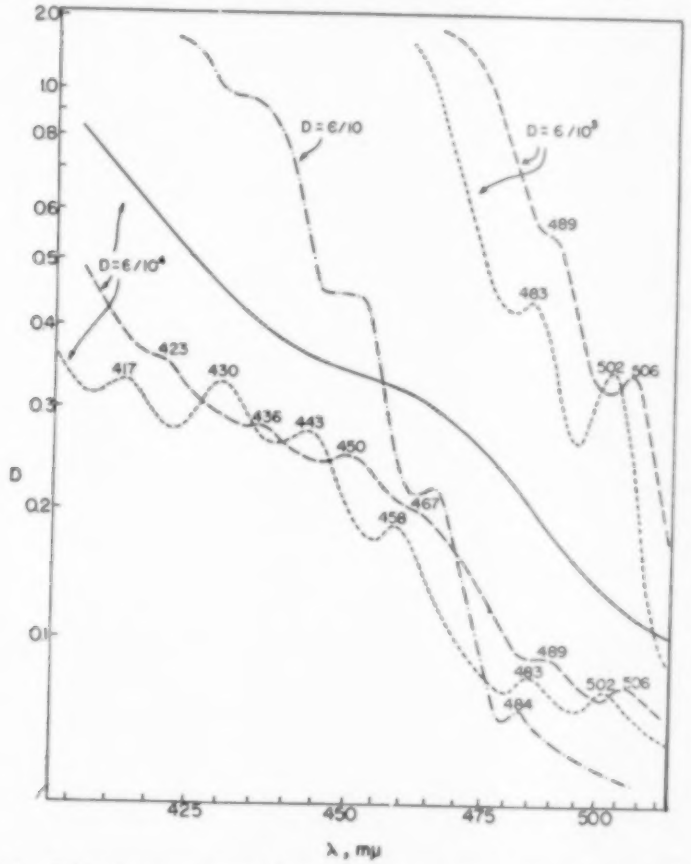

FIG. 3.—Enlarged section of uranyl chelate spectra in the visible: bisacetylacetono ——, bistrifluoroacetylacetono — — —, and bishexafluoro - - - uranyl chelates in $1{\cdot}0 \times 10^{-4}$ and $1{\cdot}0 \times 10^{-3}$ M chloroform solution. Also uranyl dinitrate hexahydrate, — · —, $1{\cdot}0 \times 10^{-1}$ M in dioxane; fresh preparation.

with the hydrate of hexafluoroacetylacetone is in agreement with the observations of HASZELDINE *et al.*[4]

The reactions of the uranyl ion with bisacetylacetoneethylenediimine did not give the simple inner complex salt of the Schiff base as did the copper(II) ion. The compound isolated was apparently a molecular complex bisacetylacetoneethylenediimine (unchelated) and uranyl bisacetylacetonate. The analytical results showed that the composition of this molecular association compound varied slightly with the conditions of crystallization. The same product was obtained when the Schiff base and the uranyl salt were the only reactants and when ethylenediamine, acetylacetone and

TABLE 1.—ABSORPTION BANDS OF $CHCl_3$ SOLUTIONS IN THE ULTRA-VIOLET AND VISIBLE REGIONS

	Compound	Molarity	λ_{max}	ϵ_{max}
I	Acetylacetone	$4{\cdot}0 \times 10^{-5}$	280	9,500
I-UO_2	Bisacetylacetono-dioxouranium(VI)	$2{\cdot}0 \times 10^{-5}$	277	21,500
		$1{\cdot}0 \times 10^{-4}$	363	1,900
			(440)	
			(470)	
II	Trifluoracetylacetone	$4{\cdot}0 \times 10^{-5}$	284	10,500
II-UO_2	Bistrifluoroacetylacetono-dioxouranium(VI)	$2{\cdot}0 \times 10^{-5}$	284	17,000*
		$1{\cdot}0 \times 10^{-4}$	360	4,200*
		$1{\cdot}0 \times 10^{-3}$	(423)	36
		$1{\cdot}0 \times 10^{-3}$	436	28
		$1{\cdot}0 \times 10^{-3}$	450	25
		$1{\cdot}0 \times 10^{-2}$	(467)	—
		$1{\cdot}0 \times 10^{-2}$	(489)	~9
		$1{\cdot}0 \times 10^{-2}$	506	~7
III	Hexafluoroacetylacetone	$4{\cdot}0 \times 10^{-5}$	273	7,800
III-UO_2	Bishexafluoroacetylacetono-dioxouranium(VI)	$2{\cdot}0 \times 10^{-5}$	290	11,500
		$2{\cdot}0 \times 10^{-5}$	310	11,000
		$1{\cdot}0 \times 10^{-4}$	364	7,300
		$1{\cdot}0 \times 10^{-3}$	417	33
		$1{\cdot}0 \times 10^{-3}$	430	33
		$1{\cdot}0 \times 10^{-3}$	443	28
		$1{\cdot}0 \times 10^{-3}$	458	18
		$1{\cdot}0 \times 10^{-3}$	483	7
		$1{\cdot}0 \times 10^{-2}$	502	6

* HASZELDINE *et al.*[5] report ϵ values of 11,500 and 4500 at 280 and 352 mμ respectively, in ethanol.

uranyl acetate were brought together simultaneously. In the former case, hydrolysis of the Schiff base apparently took place in the presence of the uranyl ion. It is suggested that this reaction occurs through preliminary formation of an unstable chelate between the uranyl ion and the tetradentate Schiff base, followed by hydrolysis as is indicated in the following chemical equation:

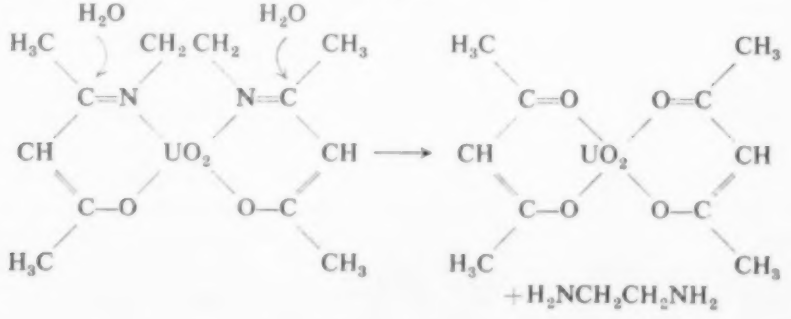

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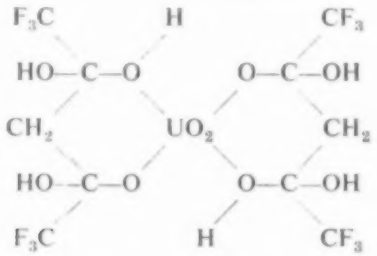
TABLE 2.—INFRA-RED ABSORPTION BANDS OF LIGANDS AND URANYL(VI) CHELATES

I	I-UO_2	II	II-UO_2	III	III-UO_2	IV	V
3550							
		3360	3360		3530		
	3100	(3120)	3200	3120	(3170)	3160	3160
2960		2980		2950			
						(2700)	(2700)
(2620)				(2580)			
				2420			
(2350)	(2340)	(2350)	(2280)			2340	2340
				(2200)			
				2000			
		1775		1790			
		1745		1765			
(1725)		(1713)					
1708		1680		1680	1650		
1620			1623	1625	(1620)		
	1580		1600			1575	1578
			1555		1568		1550
	1530		1534		1540	1530	
			1514				1520
		(1475)			1460		(1495)
		1455		1450			
1425		(1430)					
1365		1375	1368				
		1350		(1350)			
						1335	1330
1305			1300			(1315)	
						1287	
	1268	1282	1280	1270	1258	1270	1270
1252		1230	1233	1220	1210	1214	1215
	1195	1200	1192			(1195)	(1190)
							1175
	(1150)	1160	1150	1160	1145	(1150)	(1160)
			1140		1108	1112	1138
		1095		1085			1080
	1020	1030	1025		1035	1020	1016
		(990)			995	990	975
	(945)		955		945	950	955
	923		928		925	923	923
		900	912	913		910	906
			860			858	(850)
	815	822	837	819		830	827
			800		810	805	
780					775	780	785
				743	745		763
		730	727		(723)	720	725
		700					
							675
		665		655	660		650

This reaction is similar to the Cu(II)-catalysed hydrolysis of ethyl β-diethylamino-trifluorocrotonate reported previously.[1] In reactions of this type, the central metal ion serves to increase the electropositive nature of the donor nitrogen and thus speeds up the attack by a base such as water.

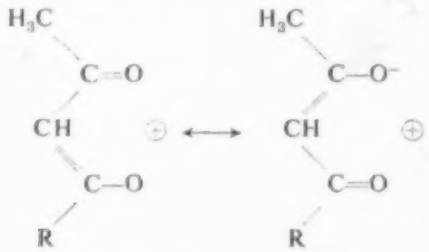
The analyses given for the uranyl chelates of acetylacetone and trifluoroacetylacetone are compatible with the presence of water of hydration, and are possibly monohydrates. This conclusion is supported by the presence of a strong hydroxyl band at 3100 cm^{-1} for the former compound, and of strong hydroxyl bands at 3200 cm^{-1} and 3360 cm^{-1}. In this connection it should be noted that all of the wide variety of β-diketone uranyl chelates prepared by SACCONI and GIANNONI[5] were found to be hydrates which could be dehydrated only with difficulty. Their observation of a deepening of colour of the chelate to red on dehydration is also similar to the behaviour observed for the acetylacetonate and for the trifluoroacetylacetonate.

The hexafluoroacetylacetono-UO_2(VI) chelate is unique in that it forms a tetrahydrate, characterized by a strong absorption band at 3530 cm^{-1}. Because of the tendency of the trifluoromethyl groups to hydrate an adjacent carbonyl group, a possible formula for the uranyl chelate is derived from a hydrated form of the β-diketone, in which two hydrogen ions are replaced by the uranyl ion.



Another possibility is one in which the water is directly associated with the uranyl ion.

Ultra-violet absorption spectra. The ultra-violet absorption spectra of the ligands have been previously described.[1] The spectra of the uranyl chelates resemble those of the ligands in that they all contain a strong band at about the same frequency as that of the ligand and are considerably intensified. These are *K*-type bands which correspond to transitions in enolate structures of the type:



Thus the ultra-violet absorption bands of the uranyl β-diketonates arise from transitions similar to those described previously for Cu(II)–β-diketone derivatives.

[5] L. SACCONI and G. GIANNONI, *J. Chem. Soc.* 2368 (1954).

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The introduction of trifluoromethyl groups in the β-diketone has two pronounced effects on the spectra: (1) it increases the splitting into a number of weaker *K*-type transitions of lower frequency; and (2) it greatly increases the intensity of the subsidiary (360 mμ) bands. Thus the spectra in Fig. 1 show two bands for bisacetylacetono-UO_2(VI), one of which is very weak. In the trifluoro chelate compound, the secondary band is much more intense, but has about the same frequency as that of the acetylacetone derivative. In the hexafluoro compound, this band is further greatly intensified, but its frequency is again not greatly changed. The latter compound also shows a third, intense *K*-type band of only slightly lower frequency (and intensity) than that of the main band. This band is evident as a weak shoulder on the side of the main absorption band of the trifluoro derivative, while so weak as not to be at all discernible in the absorption of the unfluorinated chelate.

It appears that the integrated intensity of absorption for each of the three uranyl chelates is approximately the same for the entire spectral region shown in Fig. 1. The subsidiary bands grow at the expense of the original strong enolate band. However, we lack sufficient knowledge about these transitions to state what significance this fact has.

Of two possibilities for the 360 mμ bands, charge-transfer, or ligand n-π or π-π transitions, we favour the ligand system interpretation. We are prejudiced against charge-transfer because of the insensitivity of *position* of these bands to ligand basicity. One might at first glance make the same objection to the ligand transition alternative, but spectra of the chelating agents[1] contain some ligand bands whose positions are not powerfully dependent upon substituent fluorination or ligand basicity. A more serious argument is the absence of the 360 mμ bands, at least at the same frequencies, in the parent chelating agents or their cupric chelates.[1] However, it does not follow that the OUO^{2+} group must be a primary participant in the transitions. Its imminence could influence or promote essentially ligand transitions. A third possibility exists—that the bands are transitions within the OUO^{2+} group.

The strong influence of fluorine substitution on the spectra of the uranyl β-diketones may be observed in the near ultra-violet and visible regions illustrated in Figs. 2 and 3. In the spectrum of the nitrate the many absorption bands resulting from electronic transitions of the uranyl ion are clearly visible. In the uranyl chelates, the absorption bands of the metal are superimposed on the strong tail-off of the 360 mμ band.

The visible absorption bands of the nitrate show a well-defined vibrational structure for the excited state, with an approximate separation of 750 cm^{-1}. Increased ligand basicity *appears* consistently to increase the vibrational frequency, e.g., the hexafluoro and trifluoro acetylacetonates show 795 and 812 cm^{-1}, respectively. Several authors,[6–10] report fluorescence, absorption and infra-red vibrational

[6] A. N. Sevchenko, V. M. Vdovenko, and T. V. Kovaleva, *Zh. Eksp. Teor. Fiz.* **21**, 204 (1951); *Chem. Abstr.* **46**, 2407 (1952).
[7] L. H. Jones and R. A. Penneman, *J. Chem. Phys.* **21**, 542 (1953).
[8] G. H. Dieke and A. B. F. Duncan, *Spectroscopic Properties of Uranium Compounds.* McGraw-Hill, New York (1949).
[9] E. Rabinowitch, Argonne National Laboratory Report No. ANL-5122 (1953) and several references cited there.
[10] E. Rabinowitch, Argonne National Laboratory Report No. ANL-5173 (1953) and several references cited there.

measurements for OUO^{2+} salts. The fluorescence and infra-red measurements, related to ground-state properties, show frequencies about 20 per cent higher than ours. The absorption results generally show frequencies of about 700 to 750 cm^{-1} for the symmetric stretch of OUO^{2+} in its upper electronic state. It is tempting to speculate that the more basic ligands attach themselves more securely to the uranium atom, decreasing its tendency to coordinate with extra H_2O molecules (see the analyses) and thus indirectly decreasing the effective mass and perhaps the force constant of the U—O bond. We are testing this hypothesis with further work.[11]

It is also apparent from the absorption spectra in Figs. 2 and 3 that the higher the basicity of the ligand, the stronger is the interference with, or broadening of, the visible absorptions of the metal ion. In the chelate compound formed from the most basic ligand, acetylacetone, the electronic transitions of the uranyl ion are smeared out to such an extent that they are evident only in the generally wavy nature of the absorption curve. With successive fluorination these bands sharpen up and are displaced toward higher frequencies, probably as a result of lesser alteration of the electronic energy levels of the UO_2 ion by successively weaker ligand fields. The direction of the shift is curious and merits future investigation.[11]

Infra-red spectra. The infra-red spectra of the bidentate ligands have been described in the first paper of this series, while the infra-red spectra of the tetradentate ligands have been described in the second.

In the uranyl chelate spectra there appear strong absorptions in the hydrogen-bonded hydroxyl stretch region. These, together with the analyses, serve to identify the chelates as hydrates.

The uranyl chelates of acetylacetone and its fluorinated derivatives are characterized by the absence of the normal carbonyl absorption bands found in the ligands, and by the presence of metal-chelated carbonyl bands at much lower frequencies. The absorption bands at 1580 cm^{-1} and 1530 cm^{-1} are assigned to chelated carbonyl and to C=C stretch in accordance with a similar assignment for the corresponding Cu(II) chelate[2] and in agreement with the assignments made by LECOMPTE *et al.*[12,13] As in the Cu(II) chelates there is a considerable increase in the frequency of the carbonyl band as the stability of the chelate decreases (i.e., as fluorine is substituted into the ligand), while only a slight increase in the C=C stretching frequency occurs with fluorine substitution.

The chelates believed to be molecular association compounds between uranyl acetylacetonate and the Schiff bases bisacetylacetoneethylenediimine (compounds IV and V of Table 2) show considerable resemblance to the spectra of the separate compounds. Some of the bands of the individual substances are shifted or are missing in the association compounds. The most noticeable difference is the absence of the carbonyl absorptions of the Schiff bases. The absence of these, and a few other bands, in the combined spectra is reasonable in view of the molecular interactions which must take place between the polar groups of the Schiff bases and the metal chelate.

All the uranyl chelates show some bands near 950–1000 cm^{-1}. We assign part of this absorption to OUO stretches.

[11] R. L. BELFORD and J. MUIRHEAD. To be published.
[12] J. LECOMPTE, *Disc. Faraday Soc.* No. 9, 125 (1950).
[13] C. DUVAL, R. FREYMAN and J. LECOMPTE, *Bull. Soc. Chim. Fr.*, 106 (1952).

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REACTIONS OF GROUP Vb CHLORIDES WITH BORON TRICHLORIDE AND GALLIUM TRICHLORIDE*

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Abstract—The complex, $PCl_5 \cdot GaCl_3$, was prepared. Several new procedures were developed for the synthesis of $PCl_5 \cdot BCl_3$, a knowledge of which allows an interpretation to be made concerning its mode of formation. The unusual properties exhibited upon sublimation of $PCl_5 \cdot BCl_3$ suggested a reversible dissociative process. Similar complexes did not form with chlorides of arsenic and antimony.

IN 1863 BAUDRIMONT[1] reported the formation of a white, non-volatile solid having the composition, $PCl_5 \cdot AlCl_3$. Later workers[2] after investigating the thermal properties of this compound postulated a salt-like structure, consisting of the ions PCl_4^+ and $AlCl_4^-$. A complex of similar composition has been reported[3] between phosphorus pentachloride and boron trichloride. An investigation of the latter's electrical conductance in liquid phosphorus oxychloride led more recent workers[4] to postulate an ionic structure for it, PCl_4^+ BCl^{4-}. The presence of the PCl_4^+ ion has been established in solutions of several other complexes as well as in solid phosphorus pentachloride[5] itself. Typical examples are PCl_4^+ ICl_2^-,[6,7] PCl_4^+ $SbCl_6^-$[7] and more recently PCl_4^+ PF_6^-[8] and PCl_4^+ PCl_5Br^-.[9]

One might anticipate the formation of the corresponding $AsCl_4^+$ and $SbCl_4^+$ ions. A review of the literature indicates that the $AsCl_4^+$ ion is present in $PCl_5 \cdot AsCl_5$, $SbCl_5 \cdot AsCl_5$[10] and $AsCl_4^+$ AsF_6^-[11] but at least the first two of these complexes are thermally unstable. No reports of the $SbCl_4^+$ ion have been found.

It was of interest to see if arsenic and antimony would form complexes analogous to those of phosphorus. Consequently, the reactions of chlorides of arsenic and antimony with trichlorides of boron, aluminium and gallium were studied. Gallium trichloride was included since it might be anticipated to enter into reaction with phosphorus pentachloride analogous to the chlorides of boron and aluminium (the latter point was also investigated in this study), especially in view of the recently

* Abstracted in part from a thesis submitted by R. R. HOLMES in partial fulfillment of the requirements for the degree of Doctor of Philosophy, the remainder of the work being performed at Carnegie Institute of Technology.

[1] M. E. BAUDRIMONT, *C.R. Acad. Sci., Paris* **55**, 363 (1863).
[2] W. FISCHER and O. JUBERMANN, *Z. Anorg. Chem.* **235**, 337 (1938).
[3] J. TARIBLE, *C.R. Acad. Sci., Paris* **116**, 1521 (1893).
[4] W. L. GROENEVELD and A. P. ZUUR, *Rec. Trav. Chim.* **72**, 617 (1953).
[5] H. M. POWELL, D. CLARK and A. F. WELLS, *Nature, Lond.* **145**, 149 (1940).
[6] YA. A. FIALKOV and A. A. KUZMENKO, *J. Gen. Chem. (U.S.S.R.)* **21**, 473 (1951).
[7] V. GUTMANN, *Z. Anorg. Chem.* **264**, 151 (1951).
[8] L. KOLDITZ, *Z. Anorg. Chem.* **284**, 144 (1956).
[9] L. KOLDITZ and A. FELTZ, *Z. Anorg. Chem.* **286**, 293 (1958).
[10] V. GUTMANN, *Monatsh.* **82**, 473 (1951).
[11] L. KOLDITZ, *Z. Anorg. Chem.* **280**, 313 (1955).

postulated existence of the tetrachlorogallate ion in melts of compounds such as, $COCl{\cdot}GaCl_3$[12] and $POCl_3{\cdot}GaCl_3$.[13]

In addition several new procedures were developed for the synthesis of $PCl_5{\cdot}BCl_3$ as well as an examination of its thermal behaviour to obtain information concerning the mode of formation of complexes of this type, the latter being chosen to work with because of experimental difficulties such as solubility and volatility problems encountered with both aluminium and gallium trichlorides.

EXPERIMENTAL

Materials

All materials employed in procedures not utilizing high vacuum equipment were used as supplied by the company. Reagents used in vacuum line procedures were purified just prior to performing the experiment. The following is a list of the materials so purified.

Phosphorus pentachloride (Merck) was sublimed twice in an all-glass apparatus and stored in sealed ampoules.

Antimony pentachloride (General Chemical Co.) was fractionally distilled in an all-glass apparatus, the purified product being stored in sealed ampoules.

Boron trichloride was purified by regenerating it from its nitrobenzene addition compound as described in previous work.[14] The vapour-pressure at 0° was 474 mm.

The gallium trichloride was part of a sample prepared by the action of hydrogen chloride on gallium metal in an all-glass system at 200°.

Phosphorus trichloride (Baker's Analysed) was fractionated in the vacuum line. The vapour-pressure of the purified sample was 35·1 mm at 0°.

Arsenic trichloride (Baker's Analysed) was subjected to fractionation in the vacuum line, after which its vapour-pressure was 10 mm at 26·0°.

EXPERIMENTS

Phosphorus pentachloride–boron trichloride system

Pressure composition data were determined for the phosphorus pentachloride–boron trichloride system at 0° using an apparatus previously described.[15] The resulting diagram showed no evidence for compound formation and indicated a very low solubility of solid phosphorus pentachloride in liquid boron trichloride. These reagents did react, however, under the following sets of conditions.

Procedure A. Reaction of phosphorus pentachloride and boron trichloride in carbon tetrachloride. Tank boron trichloride (Matheson) was bubbled through a 4 per cent solution of phosphorus pentachloride (4·5 g) in carbon tetrachloride (125 ml). A white precipitate formed which was filtered through a sintered-glass crucible, the operation being carried out inside a Berkeley-type gloved box filled with a dry nitrogen atmosphere, The product was washed with small portions of dry solvent, transferred to ampoules and dried by pumping off the remaining liquid. The ampoules were then sealed under vacuum.

Elemental analyses were performed by titrating the hydrolysis products. The Volhard method was used to obtain the chlorine analysis. Titration of phosphoric and boric acids with carbonate-free base gave the phosphorus and boron content. (Found: P, 9·70; B, 3·38; Cl, 85·3, Calc. for $PCl_5{\cdot}BCl_3$: P, 9·52; B, 3·32; Cl, 87·1%).

Procedure B. Reaction of phosphorus pentachloride with boron trichloride at elevated temperatures. Using the vacuum line, excess boron trichloride (3·55 mmoles) was condensed on phosphorus pentachloride (1·63 mmole) in a glass ampoule having a break tip. After sealing the ampoule from the line, a dry-ice cone was placed around the upper part of the ampoule, thus causing the boron trichloride to reflux. The lower portion of the ampoule was heated gently, causing the phosphorus pentachloride to sublime through the boron trichloride vapour. The process was repeated several times. The ampoule was then opened in the vacuum line via the break tip and the excess boron

[12] N. N. GREENWOOD and K. WADE, *J. Chem. Soc.* 1527 (1956).
[13] N. N. GREENWOOD and K. WADE, *J. Chem. Soc.* 1516 (1957).
[14] H. C. BROWN and R. R. HOLMES, *J. Amer. Chem. Soc.* **78**, 2173 (1956).
[15] H. C. BROWN and R. WONG, *J. Amer. Chem. Soc.* **75**, 6275 (1953).

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trichloride removed and measured. It was found that 1·60 mmoles of boron trichloride had reacted with 1·63 mmoles of phosphorus pentachloride, corresponding to the formation of $PCl_5 \cdot BCl_3$.

Procedure C. Chlorination of an equal molar mixture of phosphorus-trichloride and boron trichloride at −78°. A 1 : 1 mixture of boron trichloride and phosphorus trichloride was made up in a weighed ampoule connected to the vacuum line. Then the ampoule was reweighed and connected to a glass, mercury-free, vacuum apparatus. Excess chlorine was condensed in the ampoule and reaction allowed to take place at −78°. A white solid formed, insoluble in excess chlorine. The excess chlorine was transferred to a liquid nitrogen trap and the ampoule removed and reweighed. By this method of analysis, the composition of the product was found to correspond to a mole ratio of $PCl_3 : BCl_3 : Cl_2$ — 1·0 : 1·0 : 0·9. However, since this method is not very accurate, it was analysed by the method listed under Procedure A for the preparation of $PCl_5 \cdot BCl_3$. (Found: P, 9·11; B, 3·18; Cl, 87·2. Calc. for $PCl_5 \cdot BCl_3$: P, 9·52; B, 3·32; Cl, 87·1%).

Preparation of $PCl_5 \cdot AlCl_3$

No new methods were discovered for the preparation of $PCl_5 \cdot AlCl_3$ in this study. Hence, it was prepared by the method previously reported.[12] To check the composition aluminium was determined gravimetrically as the 8-hydroxyquinolate.[16] (Found Al, 7·70. Calc. 7·89%).

Preparation of $PCl_5 \cdot GaCl_3$

$PCl_5 \cdot GaCl_3$ was prepared by slowly mixing carbon tetrachloride solutions (about 4 per cent) of phosphorus pentachloride (1·44 g) and gallium trichloride (1·22 g) together, the reaction being carried out inside the dry box. A white solid formed. This was filtered through a sintered-glass crucible, washed with dry carbon tetrachloride and transferred to ampoules. The remaining solvent was pumped off and the product sealed under vacuum. About 2·25 g of the product was obtained, corresponding to a 94 per cent yield.

The compound was analysed for chlorine content and total acid. The chlorine was determined by the Volhard procedure. (Found: Cl, 73·2; total acid, 99·6. Calc. for $PCl_5 \cdot GaCl_3$: Cl, 73·8; total acid, 100·00%).

Attempts to prepare $AsCl_5 \cdot BCl_3$, $AsCl_5 \cdot GaCl_3$ *and* $SbCl_5 \cdot BCl_3$

Using the chlorination apparatus and Procedure C given above for $PCl_5 \cdot BCl_3$, an equimolar mixture of arsenic trichloride and boron trichloride was chlorinated. A miscible system was present at 0° but on removal of the volatile material at −78° the initial amount of arsenic trichloride remained, unreacted.

A similar chlorination experiment on a mixture of arsenic trichloride (4·15 mmoles) and gallium trichloride (0·950 mmole) resulted in no reaction as evidenced by the complete recovery of the initial amount of gallium trichloride used.

Pressure composition data (Table 1) of the antimony pentachloride–boron trichloride system at 12·0° obtained using an apparatus previously described[14] showed that the system exhibited positive deviations from Raoult's law (column 3 lists the ideal pressures). No reaction occurred as further evidenced by the complete recovery of boron trichloride at −78°.

The systems of arsenic trichloride with aluminium trichloride and antimony trichloride with the various Group III trichlorides are known to be immiscible[17] and were not investigated further. Also the systems of aluminium and gallium trichlorides with antimony pentachloride were found to be immiscible.

Properties of $PCl_5 \cdot MCl_3$

These compounds are white solids, easily hydrolysed by water and insoluble in reagents like carbon tetrachloride and chloroform. When attempting to dissolve them in oxygenated solvents like acetone, reaction occurs. $PCl_5 \cdot AlCl_3$ melted at 375–379°. A literature value of 343° reported by Fialkov and Bur'yanov[18] appears suspiciously low. $PCl_5 \cdot GaCl_3$ melted at 368–371° while $PCl_5 \cdot BCl_3$ sublimed completely in a sealed tube without melting at about 340°, the temperature of

[16] G. E. Lundell and H. B. Knowles, *Bur. Stand. J. Res.* **3**, 91 (1929).
[17] R. R. Holmes, *J. Inorg. Nucl. Chem.* **12**, 266 (1960).
[18] Ya. A. Fialkov and Ya. B. Bur'yanov, *Dokl. Akad. Nauk. USSR* **92**, 585 (1953).

TABLE 1.—ANTIMONY PENTACHLORIDE–BORON TRICHLORIDE SYSTEM AT 12·0

$PBCl_3$ (exptl.) (mm)	Mole fraction BCl_3	$PBCl_3$ (calc.)* (mm)
70·9	0·0504	36·9
116·7	0·0958	70·1
170·8	0·151	110
219·6	0·210	154
271·9	0·268	196
305·6	0·314	230
343·0	0·364	266
372·9	0·407	298
402·3	0·447	328
419·2	0·475	348

* $P^{\circ}(BCl_3)$ at 12·0° = 733 mm

complete sublimation varying somewhat depending on the pressure developed in the tube during the course of the sublimation. $PCl_5 \cdot BCl_3$ was found to be the most volatile of the three.

On heating a sample of $PCl_5 \cdot BCl_3$ in a sealed tube to about 300°, it sublimes from the heated portion in a matter of minutes; while under similar circumstances, the others will require 3–4 hr. The vapour of $PCl_5 \cdot BCl_3$ in the gas phase in a sealed tube at about 340° is yellow-green, indicating dissociation into chlorine, boron trichloride and phosphorus trichloride. On cooling, a white sublimate covers the entire tube and then liquifies, the vapour becoming colourless during this process. A few seconds later a white solid again coats the entire tube. On reheating the sample, the same sublimation point is observed.

DISCUSSION

The only evidence offered here which might give any indication of the type of structure that solid $PCl_5 \cdot GaCl_3$ (formed in this work) possesses is the same type of evidence upon which the structure, $PCl_4^+ AlCl_4^-$, was postulated for solid $PCl_5 \cdot AlCl_3$, i.e., similar high melting points of the complexes compared to the much lower melting points of their respective components. X-ray information for these substances is completely lacking and definite conclusions regarding their structure must be postponed. Whatever the structure of the series of solids, $PCl_5 \cdot BCl_3$, $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot GaCl_3$, it appears likely (as the comparative properties indicate) that they will all be closely related.

Since arsenic pentachloride does not exist it was hoped to find evidence for a series of complexes similar to that formed with phosphorus pentachloride by chlorinating a homogeneous mixture of arsenic trichloride and the respective Group III trichloride. However, later work* showed that the formation of even small amounts of arsenic pentachloride in such a mixture is highly improbable. Thus the fact that negative results were obtained in the chlorination experiments is no real evidence against the existence of a complex such as $AsCl_5 \cdot BCl_3$ or $AsCl_5 \cdot GaCl_3$. With antimony, however, the results of the antimony pentachloride–boron trichloride experiment indicate more definitely that a complex such as $SbCl_5 \cdot BCl_3$ does not exist.

On considering the preparative methods used to obtain $PCl_5 \cdot BCl_3$, some peculiarities arise. For example, it was found that phosphorus pentachloride was insoluble in boron trichloride at 0° but would react with it to form $PCl_5 \cdot BCl_3$, if the phosphorus

* Unpublished work: phase diagram studies of the system, arsenic trichloride-chlorine, indicate that there is no tendency for association of the components.

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pentachloride was sublimed through the boron trichloride vapour, or if the components were dissolved in a solvent such as carbon tetrachloride and then reacted. Furthermore, $PCl_5 \cdot BCl_3$ could be prepared by chlorinating a mixture of phosphorus trichloride and boron trichloride at $-78°$, even though the phosphorus trichloride does not combine with boron trichloride.[17]

It may be that phosphorus pentachloride, possessing an ionic lattice, will not react with boron trichloride in this form. However, by transforming it into the gas phase where the structure is in the form of the non-polar trigonal bipyramid, or by dissolving it in a solvent in which it has the non-polar form, it will react as observed. In the case of the formation of $PCl_5 \cdot BCl_3$ on chlorinating a mixture of phosphorus trichloride and boron trichloride, the process must be more complicated. Since phosphorus trichloride and boron trichloride do not react but phosphorus trichloride and chlorine do, the first step must involve the latter components. Since solid phosphorus pentachloride will not react with boron trichloride, the latter must enter the chlorination process when an intermediate in the reaction of phosphorus trichloride and chlorine is formed, i.e., before any solid pentachloride is produced.

It was observed on heating a sample of $PCl_5 \cdot BCl_3$ in a sealed tube to about 340° that the compound sublimed completely, the vapour being yellow-green, and on cooling reformed again, the same sublimation point being observed on repeating the process. The colour of the vapour is undoubtedly due to chlorine. If the latter is so, it would indicate that $PCl_5 \cdot BCl_3$ is dissociating reversibly into chlorine, phosphorus trichloride and boron trichloride. The above speculation seems reasonable if it is noted that above 300° phosphorus pentachloride is completely dissociated into the trichloride and chlorine. Hence, its presence is not considered in the dissociation of $PCl_5 \cdot BCl_3$ at the higher temperature. FISCHER and JUBERMANN[2] noted analogous behaviour of $PCl_5 \cdot AlCl_3$ in the region from 450 to 640°.

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HALOGEN EXCHANGE BETWEEN THORIUM(IV) IODIDE AND CARBON(IV) CHLORIDE*

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Abstract—The reaction between thorium(IV) iodide and carbon (IV) chloride at 100 or 200° has been shown to provide a carbon(IV) chloride-insoluble product from which thorium(IV) chloride may be separated in high yield. Other reaction products identified include iodine, carbon, and trichloroiodomethane. Studies relating to the composition of the initial carbon(IV) chloride-insoluble product are described and possible interpretations of the experimental data are suggested.

IN connexion with certain experiments concerned with the lower iodides of thorium[1] we observed that halogen exchange between thorium(IV) iodide and carbon(IV) chloride under anhydrous conditions is substantially complete over a period of a few days at 100°. This reaction has been investigated in considerable detail and the results are given below; particular emphasis was placed upon the use of this reaction in the synthesis of pure anhydrous thorium(IV) chloride.

Other routes to thorium(IV) chloride include direct chlorination of thorium (IV) oxide,[2,3,4,5] oxalate[4] or carbonate,[4] in the presence of carbon; direct chlorination of thorium,[6] thorium hydride[7] and thorium carbide;[4] chlorination of thorium(IV) oxide with sulphur(I) chloride and chlorine,[8,9] carbonyl chloride,[10] carbon(IV) chloride[11] or phosphorous(V) chloride;[12] and the treatment of thorium hydride with hydrogen chloride.[7]

Exchange of halogens between carbon(IV) chloride and iodides is well known, e.g., with aluminium(III) iodide,[13] calcium(II) iodide 2-hydrate,[14] boron (III) iodide,[15] lithium iodide hydrates,[16] methyl iodide[17] and ethyl iodide.[18] All of these reactions however were studied with a view to the synthesis of carbon (IV) iodide.

EXPERIMENTAL

All materials employed in this work were anhydrous reagent grade chemicals. Thorium(IV) iodide was prepared in the manner described previously.[1]

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[2] J. M. MATTHEWS, *J. Amer. Chem. Soc.* **20**, 815 (1898).
[3] J. J. BERZELIUS, *Pogg. Ann.* **16**, 385 (1829).
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Reactions between thorium(IV) iodide and carbon(IV) chloride at 100° were carried out in sealed standard wall 15 mm ID Pyrex tubes that were degassed under reduced pressure prior to use. For reactions at 200° tubes having a minimum wall thickness of 2 mm were employed. Sublimations were carried out in 20 mm ID Vycor tubes that were degassed at 800°; the samples were sublimed at 10^{-3} to 10^{-4} mm and volatile products were collected in traps cooled with dry-ice–isopropyl alcohol mixtures. Solvent extraction experiments employed a 20 mm Pyrex tube bearing a medium porosity fritted glass filter at the mid-point and tapered near each end. One end of the tube was connected to a suction filter flask by means of a ground joint; the other end was similarly connected through a ball joint to the vessel that contained the organic solvent. Samples were placed in the tube in an atmosphere of helium and the solvent was introduced through the ball-joint, by displacement of the helium in the tube. Solutions were filtered and solvents evaporated under reduced pressure. Reactions in liquid ammonia at −78° were carried out in a simple closed glass apparatus consisting of two Pyrex tubes joined by a capillary tube bearing a medium porosity fritted glass filter.

In the analysis of samples containing both chlorine and iodine, ionic halogen was determined by precipitation of the mixed silver halides followed by preferential extraction of silver chloride in aqueous ammonia. Total halogen was determined by a modification of the CHABLAY procedure[19] and covalently bonded halogen by difference. Iodine in carbon(IV) chloride solutions was determined by titration against standard sodium thiosulphate solutions using starch indicator.

Exchange between thorium(IV) *iodide and carbon*(IV) *chloride*

Known weights of ThI_4 and CCl_4 were heated under anhydrous conditions for the periods of time given in Table 1. The contents of the tubes were agitated frequently during the heating period,

TABLE 1.—HALOGEN–THORIUM RATIOS FOR CARBON(IV) CHLORIDE-INSOLUBLE PRODUCTS OF REACTIONS AT 100°

Reaction time (days)	Ionic Cl/Th	I/Th
5	3·92	0·05
5	3·86	0·01
5	3·85	0·05
5	3·94	0·01
7	3·96	0·01
12	3·85	0·03

at the end of which the tubes were opened and the solution decanted from the insoluble products. The latter were washed with CCl_4 until colourless washings resulted; the washings were combined with the original solutions. The CCl_4-insoluble products were dried *in vacuo* at room temperature and sampled in a dry box.

In a typical case, 2·940 g of ThI_4 and 25 ml of CCl_4 were heated at 100° for 7 days. The CCl_4 solution was found to contain 0·4835 g of elemental iodine, or 24 per cent of that used as ThI_4. An aliquot of this solution was evaporated to dryness to provide a small solid residue that gave a negative test for thorium. The brownish-gray* CCl_4-insoluble product (1·5759 g) did not react to form gaseous products when a sample was treated with water or dilute acids. (Found: Th, 58·5; ionic Cl, 35·4; covalent Cl, 1·8; I, trace; HNO_3-insoluble, 1·4%).† The ionic Cl/Th ratio is 3·96; the CCl_4-insoluble product accounted for by analysis is 97·1 per cent. Halogen to thorium ratios and related data are given in Table 1; X-ray diffraction data for the CCl_4-insoluble product are given in Table 2 together with data for pure $ThCl_4$ (*vide infra*).

* This appeared to be an intimate mixture of two solids, one of which was light gray in colour and present in relatively small quantity.

† This fraction was found to contain elemental carbon in an amount corresponding to 0·92 per cent of the CCl_4-insoluble product. In a series of related experiments, the carbon content of the CCl_4-insoluble product ranged from 0·70 to 1·0 per cent.

[19] E. CHABLAY, *C. R. Acad. Sci., Paris* **140**, 1272 (1905).

TABLE 2.—X-RAY DIFFRACTION DATA FOR THORIUM(IV) CHLORIDE AND FOR THE CARBON(IV) CHLORIDE-INSOLUBLE REACTION PRODUCT*

Thorium(IV) chloride		CCl_4-insoluble product	
d(Å)	I/I_0	d(Å)	I/I_0
5·75	0·55	5·60	1·00
5·52	0·85	4·26	0·90
5·25	1·00	3·38	0·70
4·72	0·30	3·16	0·70
4·59	0·30	2·79	0·10
3·53	0·25	2·64	0·90
3·27	0·35	2·39	0·60
3·13	0·20	2·24	0·90
3·02	0·30	2·18	0·90
2·63	0·65	2·09	0·20
2·39	0·65	1·87	0·10
2·32	0·20	1·76	0·40
2·25	0·25	1·71	0·20
2·15	0·65	1·66	0·40
2·09	0·35	1·59	0·40
2·02	0·65	1·40	0·20
1·95	0·40	1·33	0·30

* These data were obtained using Cu$K\alpha$ radiation, a Ni filter, tube voltage and current of 35 kV and 15mA, and an exposure time of 6 hr. Samples were diluted 10 : 1 with starch; relative intensities were estimated visually.

Pure thorium(IV) chloride was separated from the CCl_4-insoluble product by sublimation under reduced pressure. Liberation of iodine was observed at ca. 200°, sublimation of white $ThCl_4$ began at ca. 450° but most of this product was collected over the range 600–800°. A small black non-volatile residue remained at 800°; this was separated from the white sublimate in a dry box and both fractions were sampled for analysis.

In a representative experiment, 0·2173 g of the CCl_4-insoluble product yielded 2·76 mg (1·27 per cent) of elemental iodine, and 0·1955 g of pure $ThCl_4$, or 90 per cent of the sample used. (Found: Th, 62·3; Cl, 38·0; Cl/Th, 3·99. Calc. for $ThCl_4$: Th, 62·1; Cl, 37·9%). Most of the samples of the white sublimate gave X-ray diffraction data identical with those listed in Table 2 for $ThCl_4$ and which are in good agreement with the data of MOONEY.[20] However, in some independent experiments carried out under apparently identical conditions the white sublimates gave X-ray diffraction patterns identical with that for the original CCl_4-insoluble product (Table 2), despite the fact that the Cl/Th ratios for these products were substantially 4 : 1. The black non-volatile residue (8 mg or 3·7 per cent of the sample used in the sublimation) gave an X-ray diffraction pattern which was identical with that for thorium(IV) oxide and included no extraneous lines. (Found: C, 15·3; ThO_2, 84·7%). Extraction of the black residue with dilute nitric acid yielded a solution that did not contain either thorium or chlorine; the same results were obtained following treatment of the residue with sodium in liquid ammonia at −33·5°. Qualitative tests for halogens were also negative after fusion of the residue with sodium and potassium carbonates followed by extraction with dilute nitric acid.

A sample of the CCl_4-insoluble product was heated at 200° for 2 hr at 10^{-3} mm and thereafter gave an X-ray diffraction pattern that provided the following data (relative intensities in parentheses): d(Å) = 6·27 (1·00), 5·65 (0·50), 3·16 (0·30), 2·92 (0·30), 2·39 (0·10), 2·07 (0·10). However, after this sample was heated similarly at 250–260°, it gave an X-ray diffraction pattern that was in all details identical with that for pure thorium(IV) chloride (Table 2) except for a single intense line (d = 6·27 Å).

In related experiments that were otherwise identical with those described above, the reaction between ThI_4 and CCl_4 was carried out at 200°. The X-ray diffraction pattern for the resulting

[20] R. C. L. MOONEY, *Acta Cryst.* **2**, 189 (1949).

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CCl_4-insoluble product gave data substantially identical with those given above for the CCl_4-insoluble product that was formed at 100° and subsequently heated *in vacuo* at 200°. (Found: C, 0·85%; Cl/Th, 3·94).

The carbon(IV) chloride solutions from which the foregoing products were separated, together with the CCl_4 washings of the insoluble products were distilled under reduced pressure and the volatile products were separated into four fractions by collection in ice-water and dry ice-isopropyl alcohol traps. The absorption spectra of all fractions were examined over the ranges permitted by the equipment available. The still residue consisted of a small quantity of brown gummy material that did not contain either Th or Cl and a CCl_4 solution thereof did not exhibit absorption over the range 270–1100 mμ. All four of the volatile fractions exhibited strong absorption bands at 519 and 323 mμ. In the infra-red region, maxima at 5·53, 11·85 and 14·5 μ were observed.

Extraction of the carbon(IV) *chloride-insoluble product with ethanol*

In preliminary experiments, of which the following is typical, 0·2550 g of high purity $ThCl_4$ was dissolved in 20 ml of anhydrous ethanol. The resulting solution was separated from traces of ethanol-insoluble material, the filtrate was evaporated at 10^{-3} mm, dried for 1·5 days, and the residual white solid was sampled in the dry box. (Found: Th, 42·1; Cl, 25·3; C, 16·6; H, 4·30; Th : Cl : C_2H_5OH, 1·0 : 3·9 : 3·8. Calc. for $ThCl_4{\cdot}4C_2H_5OH$: Th, 41·6; Cl, 25·5; C, 17·2; H, 4·30%). X-ray diffraction data for this product are given in Table 3.

TABLE 3.—X-RAY DIFFRACTION DATA FOR $ThCl_4{\cdot}4C_2H_5OH$*

d(Å)	I/I_o	d(Å)	I/I_o
8·61	1·00	3·99	0·10
6·35	0·50	3·85	0·25
5·63	0·25	3·52	0·10
5·10	0·10	3·14	0·20
4·72	0·45	2·82	0·20

* See footnote to Table 2.

Similarly, a 0·1777 g sample of the CCl_4-insoluble product formed at 100° was treated with 20 ml of ethanol. The solid recovered from the ethanol solution was yellow-brown in colour and was found to contain 2·7% HNO_3-insoluble material. (Found: Th, 43·2; Cl, 24·1; C, 14·6; H, 3·5%; Th : Cl : C_2H_5OH, 1·0 : 3·7 : 3·3). X-ray diffraction data for this product were identical with those given in Table 3 and included no extraneous lines. The very small ethanol-insoluble fraction consisted primarily of elemental carbon and contained traces of Th and Cl.

When the CCl_4-insoluble product formed at 200° was treated as described above the Th : Cl : C_2H_5OH ratio found for the ethanol-soluble product was 1·0 : 3·6 : 2·5 and the X-ray diffraction pattern for this product was characteristic of $ThCl_4{\cdot}4C_2H_5OH$.

It is noted above that in some instances, separation of pure $ThCl_4$ by sublimation from CCl_4-insoluble products formed at 100° yielded a white sublimate for which Th : Cl = 1·0 : 4·0 but which gave an X-ray diffraction pattern characteristic not of pure $ThCl_4$ but rather of the initial CCl_4-insoluble product. When a sample of such a product was treated with ethanol, the white solid recovered from the ethanol solution gave Th : Cl : C_2H_5OH ratios of 1·0 : 3·8 : 3·3 and an X-ray diffraction pattern exclusively characteristic of $ThCl_4{\cdot}4C_2H_5OH$.

Behaviour of the carbon(IV) *chloride-insoluble product toward liquid ammonia at* −78°

The CCl_4-insoluble product reacted with anhydrous liquid ammonia at −78° without evolution of water-insoluble gases to provide a light gray and apparently amorphous ammonia-insoluble solid that contained Th, Cl and N but was not of reproducible composition. Evaporation of the solvent from the ammonia-soluble fraction yielded a yellow-gray solid which gave an X-ray diffraction pattern that provided an identification of NH_4Cl and NH_4I only. (Found: Th, 13·3; Cl, 53·9; I, 2·3; NH_4^+, 27·5%).

When a sample of pure $ThCl_4$ was treated with anhydrous ammonia under the same conditions,

the resulting ammonia-soluble product did not give an X-ray diffraction pattern characteristic of ammonium chloride.

Photochemical liberation of iodine from thorium(IV) *iodide in the presence of carbon*(IV) *chloride*

Observations made during the course of the preceding experiments suggested that the reaction between ThI_4 and CCl_4 might be photochemically induced and/or catalysed. Accordingly a few experiments were conducted with a view to determining whether the reaction occurs in the absence of light and the extent to which the rate of liberation of elemental iodine is dependent upon illumination. In view of the essentially heterogeneous nature of the system involved, reproducible rate data were neither anticipated nor realized.

Samples of pure ThI_4 of the order of 100–150 mg in 10 ml of CCl_4 were vigorously agitated with a magnetic stirrer in closed containers for 45 min at 27 ± 1° in the dark, in ultra-violet light provided by the hydrogen discharge lamp from a model DU spectrophotometer, and in direct sunlight. The elemental iodine liberated was measured, following filtration, by titration with standard sodium thiosulphate solution. For these three conditions of illumination, I_2 liberated (g × 10^4)/g ThI_4 amounted to ca. 10, 25 and 60, respectively.

DISCUSSION

The results reported above show that the reaction between ThI_4 and CCl_4 proceeds at a measurable rate in the absence of light at room temperature and that the rate of liberation of elemental iodine is enhanced by ultra-violet light or direct sunlight. Although there are many possible reactions that can be suggested to account for part or all of the free iodine found, some reaction of the type

$$ThI_4 \rightarrow ThI_3 + I \qquad (1a)$$

$$I + I \rightarrow I_2 \qquad (1b)$$

must be invoked to account for iodine that cannot be attributed to other processes. The observed products otherwise can be accounted for by the reactions,

$$ThI_4 + CCl_4 \rightarrow ThCl_4 + CI_4 \qquad (2a)$$

$$CI_4 \rightarrow C + 2I_2 \qquad (2b)$$

$$ThI_4 + 4CCl_4 \rightarrow ThCl_4 + 4CCl_3I \qquad (3)$$

Of the iodine used as ThI_4, 24 per cent was present as elemental iodine at the end of the reaction and the remainder was present in combined form either in solution or adsorbed, or otherwise incorporated, in the CCl_4-insoluble product. It is also evident, from the quantities of elemental carbon in the insoluble product and the *total* free iodine in solution, that ca. 78 per cent of the elemental iodine resulted from reaction (2); hence, the remainder must arise from reactions of the type represented by (1). The data also indicate that about 19 per cent of the ThI_4 reacted in accordance with (2a).

Elemental carbon remaining following sublimation of the CCl_4-insoluble product accounts for 62 per cent of the total carbon present in that product. The remainder must be attributed to adsorbed or occluded volatile halogenated carbon compounds, a wide variety of which is possible under the prevailing experimental conditions. Although efforts were made to distinguish between ionic and covalently bonded halogens in these products, not too much significance can be attached to these data in view of the relatively small quantities of carbon compounds present. Related efforts to identify carbon compounds in the CCl_4 solutions on the basis of their absorption spectra were also only partially successful. The band at 519 mμ is clearly

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attributable to iodine[21] and that at 323 mμ to trichloroiodomethane.[22] We have been unable to correlate the absorption bands in the infra-red with any known carbon compounds.*

Reaction (2a) is of course subject to the criticism that pure $ThCl_4$ is not necessarily present as such in the initial CCl_4-insoluble products. The latter gave Cl : Th ratios that ranged from 3·85 to 3·96. The corresponding X-ray diffraction patterns were all closely similar but not characteristic of $ThCl_4$. Although most of the CCl_4-insoluble product was accounted for by $ThCl_4$ separated by sublimation, this procedure in some instances provided a sublimate that corresponded analytically to $ThCl_4$ but gave an X-ray diffraction pattern closely similar to those for the unsublimed CCl_4-insoluble material. In view of the data presented above, the possibility of initial formation of a distorted $ThCl_4$ lattice is unattractive; the possibility of an enantiomorph is by no means eliminated. That the CCl_4-insoluble product does not consist of $ThCl_4$ is further substantiated by the ammonolysis experiments. The present results confirm the report by FOWLES and POLLARD[6] that $ThCl_4$ is not ammonolysed by liquid ammonia at −36°. The foregoing results however show that the CCl_4-insoluble product ammonolyses extensively even at −78°. Finally, the presence of ThO_2 in the sublimation residues must be attributed to attack of the glass container by the $ThCl_4$ at the elevated temperatures employed (i.e., up to 800°).

Efforts to gain additional information relative to the composition of the CCl_4-insoluble product by selective extraction with ethanol led only to the identification of $ThCl_4 \cdot 4C_2H_5OH$. This product is apparently identical with that reported earlier.[23] The composition of the products isolated is strongly suggestive of at least a partial solvolysis,

$$ThCl_4 + xC_2H_5OH \rightarrow ThCl_{(4-x)}(C_2H_5O)_x + xHCl \qquad (4)$$

in a manner strictly analogous to the solvolysis of the chlorides of zirconium (IV) and hafnium (IV) by methanol.[24] The compound $ThCl_4 \cdot 4C_2H_5OH$ was however a component of all of the reaction products isolated from the ethanol solutions. Thus it must be concluded that the species that reacts solvolytically in the sense of equation (4) must not be pure $ThCl_4$ but rather its precursor, just as in the sublimation process.

* In experiments not reported here, use of gas chromatography in related efforts to identify halogen compounds of carbon in the CCl_4 solutions led to negative results.

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THE PREPARATION OF STIBINE AND THE MEASUREMENT OF ITS VAPOUR PRESSURE*

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Abstract—By the addition of aqueous hydroborate to solutions of antimony trichloride, stibine has been obtained in 25 per cent yield (based on hydroborate). The vapour pressure of stibine has been measured over the temperature interval 177–250°K and the data have been subjected to a thermodynamic analysis.

THE PREPARATION OF STIBINE

IN AN EXPLORATORY study of the reduction of aqueous antimony(III) solutions by large excesses of aqueous hydroborate, KRAMER§ was able to convert as much as 10 per cent of the antimony to stibine. Since we wished to explore the practicality of preparing relatively large quantities of stibine by this reaction, we sought experimental conditions for which the percentage yield of stibine *based on the hydroborate consumed* was a maximum. Good yields of stannane[3] and germane[4] have been obtained by adding hydroborate to solutions of tin(II) and germanium(IV) containing chloride or bromide. Similarly, we added hydroborate to solutions of antimony trichloride containing sufficient hydrochloric acid and sodium chloride to prevent the precipitation of basic antimony chlorides.‖

In these solutions the antimony was presumably present as some complex[5] such as $SbCl_4^-$; we therefore write, for the stibine-producing reaction, the following equation:

$$3BH_4^- + 4SbCl_4^- + 9H_2O \rightarrow 3H_3BO_3 + 4SbH_3 + 9H^+ + 16Cl^- \qquad (1)$$

We tried to minimize the various side reactions such as the hydrolysis of hydroborate to molecular hydrogen and the reactions leading to metallic antimony. A number of experimental conditions were systematically varied in an attempt to find the optimum conditions for the synthesis. The more significant observations are discussed in the following four paragraphs.

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** Most of this paper is from the Master's thesis of L. BERKA[1]. The reader is referred to this publication for detailed experimental data. (Available for $1.50 from The Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C.)

‡ Work performed in partial satisfaction of the Bachelor of Science Degree, University of California.

§ KRAMER[2], working with Prof. G. W. SCHAEFFER, added sodium hydroborate (in twenty-nine-fold excess) to acidic solutions of potassium antimony tartrate.

‖ The sum of the HCl and NaCl molarities was always 4·0 M.

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[5] J. BJERRUM, G. SCHWARZENBACH and L. SILLEN, *Stability Constants* Part II, p. 108. Chemical Society, London (1958).

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(1) The yield was markedly improved by vigorously flushing the reaction vessel with hydrogen during the addition of the hydroborate. Presumably the hydrogen served to quickly remove the stibine from the antimony(III) solution, thus preventing its oxidation to antimony metal:

$$SbH_3 + SbCl_4^- \rightarrow 2Sb + 3H^+ + 4Cl^- \qquad (2)$$

(2) When the reaction vessel was vigorously flushed with hydrogen, the yield of stibine increased with increasing concentration of antimony(III). This result may be explained in terms of the competition of the hydrogen ion and antimony(III) for the hydroborate ion. Without hydrogen flushing, the yield of stibine decreased with increasing concentration of antimony(III). Reaction (2) probably accounts for this result.

(3) The hydrolysis of hydroborate is known to be first order in hydrogen ion concentration,[6] and so one might expect better yields of stibine at lower concentrations of hydrochloric acid. This conclusion is in agreement with our findings over the concentration range 0·5–4·0 M, but we were unable to reduce the hydrogen ion concentration below 0·5 M without causing basic antimony chlorides to precipitate.

(4) In one experiment, the acidic antimony(III) solution was added to the hydroborate solution. As one might expect, the yield on the basis of antimony was fairly high (30 per cent), but the yield on the basis of hydroborate was low (7 per cent).

Under our best experimental conditions (see Experimental), we were able to obtain stibine in yields around 25 per cent of that theoretically obtainable from the hydroborate consumed.*

VAPOUR PRESSURE MEASUREMENTS

All of our stibine samples had similar vapour pressures which differed by at least 10 per cent from the literature values.[7] Even a rigorous scheme of physical and chemical methods of purification failed to reduce the discrepancy. Therefore, in addition to the synthetic investigation, we spent considerable time measuring what we believe to be a more accurate set of vapour pressures.

Two types of measurements attest the purity of our samples of stibine. The first and last fractions from trap-to-trap distillations had vapour pressures which agreed within 0·4 per cent. And, when samples were decomposed to the elements, $100 \pm 0{\cdot}2$ per cent of the theoretical amount of hydrogen was found. On the other hand, our observed melting point, $178{\cdot}9 \pm 0{\cdot}3$°K (obtained with two samples by two different methods), is distinctly lower than the previously reported values, 181·7°,[8] 185°[9] and 183·2°K.[7] We have no explanation for the discrepancy.

We wished to express our vapour pressure data in terms of a thermodynamically significant equation of the type

$$\Delta F^\circ = \Delta H_0^\circ - \Delta C_P^\circ T \ln T + IT \qquad (3)$$

where ΔF° is the free energy of vaporization, ΔC_P° is the change in heat capacity on

* In a very recent investigation (to be published), yields of 50 per cent have been obtained by adding an alkaline solution of antimonate and hydroborate to aqueous acid.

[6] R. L. Pecsok, *J. Amer. Chem. Soc.* **75**, 2863 (1953).
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[9] A. Stock and W. Doht, *Ber. Disch. Chem. Ges.* **35**, 2270 (1902).

vaporization, and ΔH_0° and I are empirical constants. Hence, it was necessary that we convert our vapour pressures into vapour fugacities. For this purpose we adapted an equation given by Brewer and Searcy[10] which permits one to estimate the ratio of fugacity to pressure for a vapour near its condensation point:*

$$f/P = 1 - [0{\cdot}0158PV_l/T]\,[(7{\cdot}78T_b/T) - 1] \tag{4}$$

Here f and P are the fugacity and pressure, respectively, in atmospheres, V_l is the molar volume of the condensed liquid in millilitres, T_b is the boiling point in °K and T is the temperature in °K. For a vapour in equilibrium with its liquid, changes in P are much greater than the corresponding changes in either V_l or T. Hence, by using average values for V_l and T (56 ml and 243°K), we were able to simplify equation (4) to

$$f/P = 1 - 0{\cdot}026P \tag{5}$$

Since the quantity $0{\cdot}026P$ was always much less than unity, we were justified in writing the more useful relation

$$\ln f = \ln P - 0{\cdot}026P \tag{6}$$

By extrapolating the heat capacity data for phosphine[12] and arsine,[13] we estimated $\Delta C_P^\circ = -6{\cdot}2$ cal degree^{-1} mole^{-1} for stibine. The constants ΔH_0° and I were evaluated by a least-squares treatment of our data. The pertinent equations are given below.

$$\Delta F^\circ = 6619{\cdot}2 + 6{\cdot}2T \ln T - 60{\cdot}28T \text{ (cal mole}^{-1}\text{)} \tag{7}$$

$$\log P_{mm} = 1{\cdot}48 \times 10^{-5}P_{mm} - 1446{\cdot}34/T - 3{\cdot}1200 \log T + 16{\cdot}0522 \tag{8}$$

$$\Delta H^\circ = 6619{\cdot}2 - 6{\cdot}2T \text{ (cal mole}^{-1}\text{)} \tag{9}$$

$$\Delta S^\circ = 54{\cdot}08 - 6{\cdot}2 \ln T \text{ (cal degree}^{-1} \text{ mole}^{-1}\text{)} \tag{10}$$

We calculate a boiling point of 254·8°K and a Trouton's constant ($\Delta H^\circ/T_b$) of 19·8.

EXPERIMENTAL

Synthesis

Yields between 20 and 30 per cent (based on hydroborate) were obtained by the following procedure. A solution which was 1·0 M in $SbCl_3$, 0·5 M in HCl and 3·5 M in NaCl was placed in a three-neck round-bottomed flask equipped with a magnetic stirrer, a hydrogen inlet tube (dipping beneath the solution), a pressure-equalized dropping funnel and an outlet tube with a dry-ice cold finger. The flask was immersed in an ice-bath. The outlet tube led, successively, to a dry-ice trap, an efficient liquid nitrogen trap, and a mercury bubbler. While stirring, and with a vigorous stream of hydrogen passing through the apparatus, a solution which was 0·5 M in KBH_4 and 0·01 M in KOH was slowly added through the dropping funnel. No more than about 200 ml of hydroborate solution should be added for every 100 ml of antimony(III) solution, since further addition of hydroborate causes negligible stibine evolution. It is important that the hydroborate solution be added slowly (about 3 ml/min) and that a fast flow of hydrogen be maintained (about 750 ml/min), or stibine may condense

* Stock and Guttmann[11], reported a molar volume for stibine gas of 23,530 ml at 288·2°K and 754 mm pressure. Using this datum and the well-known relation $f/P = PVg/RT$, we calculate $f/P = 0{\cdot}987$. By assuming that $V = 59{\cdot}4$ ml and that $T_b = 255$°K, we calculate from equation (4) that $f/P = 0{\cdot}981$ for the same temperature and pressure. The agreement of these two methods gives us confidence in equation (4).

[10] L. Brewer and A. W. Searcy, *J. Chem. Educ.* **26**, 548 (1949).
[11] A. Stock and O. Guttmann, *Ber. Dtsch. Chem. Ges.* **37**, 885 (1904).
[12] C. C. Stephenson and W. F. Giauque, *J. Chem. Phys.* **5**, 149 (1937).
[13] R. H. Sherman and W. F. Giauque, *J. Amer. Chem. Soc.* **77**, 2154 (1955).

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in the dry-ice trap. Alternatively, the reaction may be run under reduced pressure or a warmer trap may be used. We found it expedient to partially fill our liquid nitrogen-cooled trap with glass beads in order to efficiently trap out the stibine.

Essentially continuous operation of this process was made possible by providing the reaction vessel with an inlet for fresh antimony(III) solution and an outlet for spent solution. Experiments with this type apparatus showed that practically unlimited amounts of stibine could be prepared without interruption.

Before measuring the yields of our stibine preparations, the samples were distilled through a dry-ice trap *in vacuo*.

Purification

The stibine was allowed to distill slowly into three traps in series, maintained at −95°, −126° and −196°. The small amount of material (about 10 per cent of the total) which collected in the −95° and −196° traps was discarded. The remaining stibine was presumably free of impurities such as water, carbon dioxide and hydrogen chloride. In fact, we recommend the preceding purification scheme as adequate for most purposes. However, to make doubly sure that we had removed all traces of acidic impurities, we mixed the stibine with a small amount of pure liquid ammonia in a trap at −78°. While holding the trap at −78°, the mixture was connected to the pump through a trap containing magnesium perchlorate at 0° and a liquid nitrogen trap. The stibine which collected in the liquid nitrogen trap was then held at −64° and fractionally distilled by allowing the vapour to diffuse slowly through a partially opened cock to a trap cooled to −196°. The vapour pressures of the first and last 10 per cent of distillate were then measured at the temperature of melting chloroform. In two such experiments these pressures differed by less than 0·4 per cent. The middle 80 per cent of the distillate was used for analysis, melting point measurements, and vapour pressure measurements.

When stibine at pressures greater than two-thirds of an atmosphere is heated, it decomposes explosively into the elements. Two samples (measured by weight) gave 99·90 and 99·85 per cent of the theoretical amount of hydrogen.

Two procedures were used for determining the triple point temperature. One was the standard procedure described by STOCK.[16] The other involved determining the triple-point pressure by following the pressure of a sample as it was slowly warmed up through its triple-point temperature. The triple point temperature was then calculated from the triple-point pressure by means of equation (8). Five determinations by these procedures gave triple point temperatures which fell within the range 178·6–179·0 K.

TABLE 1.—THE VAPOUR PRESSURE OF STIBINE

T (K)	Observed vapour pressure (mm)			Calc. vapour pressure (mm)
	Sample A	Sample B	Average	
250·18	621·1	621·7	621·4	627·8
227·66	223·3	223·5	223·4	222·7
221·73	164·2	—	164·2	163·2
209·21	80·3	80·1	80·2	79·4
194·70	30·4	—	30·4	30·3
192·49	—	25·4	25·4	25·8
187·83	18·2	17·8	18·0	18·1
177·87	8·4*	7·9*	8·2*	—

* Solid stibine.

Vapour pressures

The vapour pressures of two different samples of stibine were determined at the temperatures provided by the following cold baths: carbon tetrachloride slush, liquid ammonia, chlorobenzene

[16] A. STOCK, *Hydrides of Boron and Silicon* pp. 183–4. Cornell University Press, Ithaca, New York (1933).

slush, chloroform slush, dry-ice–acetone, ethyl acetate slush, and toluene slush. Temperatures were determined by measuring the vapour pressures of sulphur dioxide, ammonia and carbon dioxide. The literature vapour pressure equations[15] were corrected to the temperature scale where 0 C = 273·15 K. Measurements were made with a calibrated cathetometer. The raw data were corrected for differences in the height of the mercury menisci, for the difference in the density of mercury between room temperature and 0 C, and for the local gravitational constant. When necessary, corrections were made for the presence of hydrogen due to stibine decomposition. The measured vapour pressures and the vapour pressures calculated from equation (8) are given in Table 1.

For routine vapour pressure checks, we recommend a chloroform or chlorobenzene slush, for which the uncorrected vapour pressures are approximately 81 mm or 224 mm, respectively.

[15] For SO_2: W. F. Giauque and C. C. Stephenson, *J. Amer. Chem. Soc.* **60**, 1389 (1938); for NH_3: G. T. Armstrong, *A Critical Review of the Literature Relating to the Vapour Pressure of Ammonia and Trideuteroammonia*. N.B.S. Report No. 2626; for CO_2: W. F. Giauque and C. J. Egan, *J. Chem. Phys.* **5**, 45 (1937).

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THE REACTION OF ETHYLENE WITH TETRABORANE: THE PREPARATION, STRUCTURE AND PROPERTIES OF DIMETHYLENETETRABORANE

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Abstract – The new compound, dimethylenetetraborane, $C_2H_4B_4H_8$, has been prepared in 70 per cent yields by the reaction of ethylene with tetraborane. Chemical and physical evidence indicate that it has a cyclic bridged structure which is unique in borane chemistry.

THE reaction of diborane with ethylene has been examined in detail.[1,2] However, since no study has been reported dealing with the reaction of unsaturated hydrocarbons with higher boron hydrides, it appeared of interest to explore the reaction of ethylene with tetraborane.

EXPERIMENTAL

Materials and apparatus

The tetraborane was prepared and purified according to the method described by KLEIN *et al.*[3] The ethylene (Ohio Chemical Company, U.S.P.) was purified by a slow distillation from a $-78°$C trap through a $-126°$ trap to remove less volatile material. The distillate was then distilled through a $-196°$ trap with pumping to remove more volatile impurities. The resulting condensate was tensiometrically homogeneous, exerting a vapour pressure of 459 mm at $-112°$. Infra-red examination also confirmed the purity of this material.

All of the preparations, purifications, and analyses were carried out in a conventional high vacuum line[4] (10^{-5} mm) whenever possible. The hot-cold tube reactor (volume = 400 ml) has been described previously.[3] The spectra were taken on a Perkin–Elmer Model 21 infra-red spectrometer using sodium chloride or lithium fluoride optics. A 10 cm gas cell filled to about 35 mm pressure was found to give the best results.

Preparation and purification of dimethylenetetraborane

The first attempts to induce a reaction between ethylene and tetraborane involved the rapid distillation of a mixture of the two gases through a heated reactor. No reaction occurred up to 100° either in the presence or absence of aluminium chloride. A slow distillation of tetraborane through a 220 mm atmosphere of ethylene in the reactor produced a small amount of an exceedingly unstable product. A number of static experiments in which ethylene and tetraborane were sealed in bombs at up to 30 lb in^{-2} at room temperature also produced little reaction and no alkylated tetraboranes.

In all of these early experiments the reaction seemed to occur only under conditions in which the tetraborane decomposed. This, coupled with the fact that the alkylated product appeared to be more unstable than tetraborane, suggested that a hot-cold reactor could be used to carry out the reaction. The reaction conditions were varied in an attempt to define the optimum conditions for

[1] D. T. HURD, *J. Amer. Chem. Soc.* **70**, 2053 (1948).
[2] A. T. WHATLEY and R. N. PEASE, *J. Amer. Chem. Soc.* **76**, 835 (1954).
[3] M. J. KLEIN, B. C. HARRISON and I. SOLOMON, *J. Amer. Chem. Soc.* **80**, 4149 (1958).
[4] R. T. SANDERSON, *Vacuum Manipulation of Volatile Compounds*. John Wiley, New York (1948).

the preparation. These data are summarized in Table 1. The first ten experiments were carried out using aluminium chloride as a catalyst, because it has been suggested[15] that this type of reaction proceeds by a mechanism similar to one favoured for Friedel–Crafts polymerizations. Comparison of runs (10) and (11) illustrates this effect. Under identical conditions, more product was produced in 60 min with the catalyst than in 90 min without it.

TABLE 1.—ETHYLENE–TETRABORANE REACTION IN HOT–COLD TUBE REACTOR

Run	Initial pressure (mm)	Time (min)	Temperature (°C)		$C_2H_4B_4H_8$ produced (ml)
			Hot tube	Cold tube	
HCR-1	550	60	60–70	−23	7·0
HCR-2	505	120	60–70	−23	7·8
HCR-3	490	30	60–70	23	5·5
HCR-4	470	45	60–70	23	4·0
HCR-5	540	60	60–70	−30	1·8
HCR-6	530	90	60–70	−30	4·4
HCR-7	510	20	60–70	0	3·7
HCR-8	495	60	60–70	0	13·7
HCR-9	525	60	60–70	0	26·2
HCR-10	550	60	60–70	0	29·0§
HCR-11*	550	90	60–70	0	27·4
HCR-12*	520	90†	60–70	0	28·8
HCR-13*	610	30	100	0	74·0
HCR-14*	700	40	100	0	80·5
HCR-15*	700	160‡	100	0	358

* $AlCl_3$ catalyst omitted.

† H_2 removed at 30 min intervals.

‡ Four 40 min runs identical to HCR-14.

§ The total quantity of tetraborane consumed in the first ten runs was 148 ml. The total amount of product produced was 103·1 ml, indicating an overall yield of 70 per cent.

The optimum temperature conditions for the laboratory preparation of dimethylenetetraborane, as obtained from this study, are hot temperature 100° and cold temperature −0°. As can be seen from Table 1, lowering either of these temperatures reduces the conversion, while raising them results in extensive decomposition of the product. In every case, the reaction was accompanied by a pressure decrease which was followed by a pressure increase. The best yields were obtained when the reaction was stopped after it reached a minimum pressure. The reaction times of the last eight runs were determined by this factor. This observation can be explained by the fact that initially the reactor contains liquid tetraborane at 0°. The total pressure is therefore the vapour pressure of tetraborane (388 mm) plus the ethylene pressure.

As the reaction proceeds, the ethylene is consumed and one mole of hydrogen is evolved. This would not result in a net change in pressure. However, the product, which has a vapour pressure of 14·5 mm at 0°, is forming and dissolving in the tetraborane, and this would tend to lower the total pressure in the system. As subsequent hydrogen-producing decomposition reactions begin to take place, this effect would soon be overcome and the total pressure would start to rise. The variation of initial pressure, Table 1, represents a variation in ethylene pressure and it is seen that the conversion is directly related to the initial pressure. The use of the aluminium chloride catalyst was discontinued in the last five experiments, since the increase in conversion did not appear to justify the handling difficulties.

The following procedure was most convenient and gave the best results. A liquid nitrogen bath was placed on the outer tube, and the reactants, about 480 ml of tetraborane and 130 ml of ethylene,

[15] F. G. A. STONE and W. A. G. GRAHAM, *Chem. & Ind.* 1181 (1955).

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were distilled into the reactor. The reactor was then shut off from the vacuum line, the liquid nitrogen bath was replaced with a 0° bath, and the reactor was brought up to pressure. The inner tube was filled with ethylene glycol, and this bath was heated to 100° with a knife heater to initiate the reaction. As mentioned earlier, the pressure begins to fall within a few minutes. When the pressure reached a minimum, the reaction was stopped by replacing the ice-bath with a liquid nitrogen-bath and draining the hot glycol from the inner tube.

The products were then distilled into the vacuum line through a −126° bath. This distillate was unreacted ethylene and contained only traces of diborane. The condensate was then distilled through a −90° bath to remove the bulk of the unreacted tetraborane. The last traces of tetraborane were removed by repeated distillations through a −63° bath. The condensate from this distillation was then freed of any less volatile material by distillation through a −23° bath. A repeat of the −63° distillation on the distillate then produced a condensate which was tensiometrically homogeneous, exerting a vapour pressure of 14·5 mm at 0°. The pure product was a clear liquid which did not freeze at −78°. At lower temperatures it formed a glass which did not melt reproducibly.

Product analysis

A 15·3 ml sample of the purified product exerted a pressure of 36 mm in a 352 ml standard volume at 25°, and weighed 0·0541 g, thus indicating a molecular weight of 79·2 compared to 79·3 calculated for $C_2H_4B_4H_8$. A 15·3 ml sample of the product was treated with a water–dioxane mixture and the resulting solution was oxidized with 30 per cent hydrogen peroxide and titrated. A total of 2·675 milliequivalents (meq) of boric acid was found indicating 3·8 boron atoms per molecule. Another sample of the product, 36·5 ml, was hydrolysed and oxidized in a similar manner. The resulting solution was then cooled and treated with sodium borohydride to remove any excess hydrogen peroxide. This latter step was necessary because hydrogen peroxide interferes with the fuchsin aldehyde test[6] for ethylene glycol. The solution yielded a positive test, while solutions obtained from the similar treatment of triethylboron and the various ethyldiboranes yielded negative tests. A 10·8 ml sample of the product was treated with excess methanol. The amount of hydrogen formed was 100·3 ml, indicating a ratio of 9·3, compared with the expected 9·0, equation (1).

$$C_2H_4B_4H_8 + 10CH_3OH \rightarrow (CH_2O)_2BCH_2B(OCH_3)_2 + 9H_2 \quad (1)$$

Distillation of the product of this reaction through a 30° trap produced a condensate which exerted a vapour pressure of 2 mm at 28·5°. A sample of this material was hydrolysed, oxidized, and titrated for boron. A value of 13·9 per cent boron was found, compared to 12·4 per cent calculated for $(CH_2O)_2BCH_2CH_2B(OCH_3)_2$.

DISCUSSION

The experimental evidence indicated that a mono-alkylated derivative of tetraborane had been formed. The infra-red spectrum of the product is given in Fig. 1. Except for the appearance of bands due to C—H and B—C bonds, the spectrum is

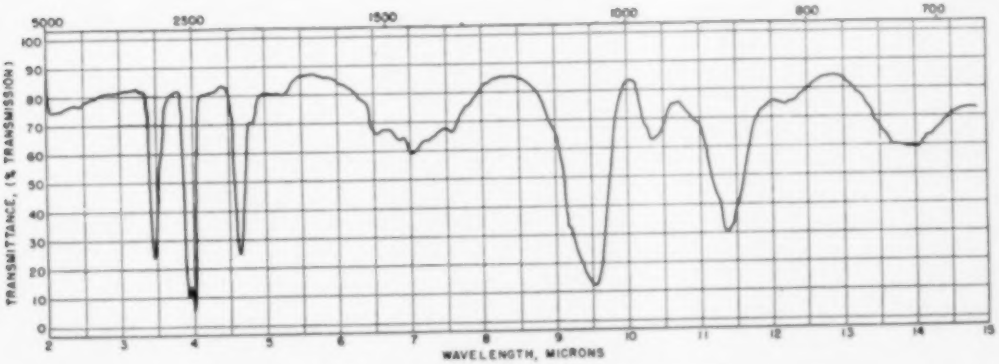
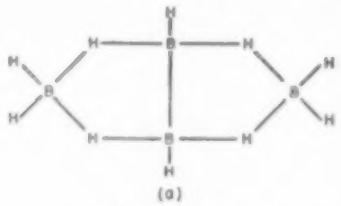


FIG. 1.—Infra-red spectrum of dimethylenetetraborane.

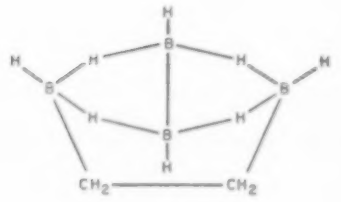
[6] F. FEIGL, *Spot Tests* Vol. II. Elsevier, New York (1954).

very similar to that of tetraborane.[7] Substitution is evidenced by the shift of B—H—B absorption from 4·71 to 4·65μ and the B—H doublet shift from 3·93 and 4·06μ, to 3·92 and 4·00μ. The most striking difference between the spectrum shown in Fig. 1 and that of tetraborane is the complete lack of absorption in the 8–9μ region in the former. Diborane, its monsubstituted and unsymmetrical disubstituted derivatives and pentaborane-11 also exhibit strong peaks in this region,[8] while other substituted



(a)

TETRABORANE



(b)

BRIDGED DIMETHYLENETETRABORANE

(c)

GEOMETRICAL REPRESENTATION
OF DIMETHYLENETETRABORANE

FIG. 2.—Structure of tetraborane and dimethylenetetraborane.

diboranes, pentaborane-9, and decaborane do not.[7] All of these observations can be explained by assigning the absorption in this region to BH_2 groups. KELLER and JOHNSTON[9] had previously indicated that this could be expected. This was an indication that there were no BH_2 groups in the product. The B—H doublet near 4μ has also been ascribed to the BH_2 group[8,10] and becomes a singlet when only B—H bonds are present. It is believed that the small indication of a doublet in Fig. 1 is due to the two different kinds of B—H bonds in the substituted molecule, because all of the other evidence supports a bridged structure containing no BH_2 groups.

[7] L. V. MCCARTY, G. C. SMITH, and R. S. MCDONALD, *Analyt. Chem.* **26**, 1027 (1954).
[8] I. J. SOLOMON, M. J. KLEIN, and K. HATTORI, *J. Amer. Chem. Soc.* **80**, 4520 (1958).
[9] W. E. KELLER and H. L. JOHNSTON, *J. Chem. Phys.* **20**, 1749 (1952).
[10] I. SHAPIRO, C. O. WILSON and W. J. LEHMANN, *J. Chem. Phys.* **29**, 237 (1958).

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The structure of tetraborane is given in Fig. 2(a). There does not appear to be any simple way of eliminating both BH_2 groups with the addition of one alkyl group to the tetraborane molecule. The fact that hydrogen was formed during all of the alkylations runs had initially been interpreted to mean that thermal decomposition reactions were taking place simultaneously. The infra-red data, however, suggested greater significance. Some typical results showing hydrogen and product formation are given in Table 2.

TABLE 2.—HYDROGEN FORMATION IN TETRABORANE–ETHYLENE REACTION

Run	H_2 (ml)	$C_2H_4B_4H_8$ (ml)
SB-1	1·6	1·9
SB-2	1·8	1·1
HCR-2	6·3	7·8
HCR-4	5·0	4·0
HCR-10	35·0	29·0
HCR-13	70·0	74·0

The data indicate that hydrogen and the alkylated product are formed in equimolar quantities. To rationalize this with the infra-red spectrum of the product, the hydrogen must come from the two BH_2 groups of the tetraborane, one atom from each, to account for the absence of BH_2 in the product. The reaction given in equation (2), therefore, could represent the system, and the bridged dimethylene structure shown in Fig. (2b) and represented geometrically in Fig. 2(c) would satisfy all of the experimental data. Such a structure is entirely consistent with the bond angles and bond distances.

$$C_2H_4 + B_4H_{10} \rightarrow C_2H_4B_4H_8 + H_2 \qquad (2)$$

The proposed structure contains two CH_2 groups. It has been observed[11,12] that the C—H bond at 3·4μ can be resolved, using lithium fluoride optics, into a series of peaks which may be used to distinguish between these two groups. The general statement can be made that the CH_3 group has a well defined peak at 3·37–3·88 μ, while absorption due to CH_2 occurs principally at 3·41–3·43μ. It has also been found in this laboratory that the shape of the resolved ethyl group band is unique, consisting of three peaks which decrease in intensity toward higher wavelengths. The resolved spectrum of the 3·4 μ band of dimethylenetetraborane is shown in Fig. 3. The structure of this band was quite different from that observed in this laboratory for ethyldiboranes. The peak usually observed at 3·37μ was absent (broken line) and the major peak occurred at 3·41 μ, indicating that only CH_2 groups were present.

Two qualitative chemical approaches to the structure of dimethylenetetraborane have also lent support to the proposed structure. The oxidative hydrolysis of dimethylenetetraborane produced ethylene glycol, equation (3), which was not detected in similar degradations with triethylborane or ethyldiboranes.

$$C_2H_4B_4H_8 + 10H_2O \rightarrow HOCH_2CH_2OH + 4B(OH)_3 + 9H_2 \qquad (3)$$

[11] J. J. FOX and A. E. MARTIN, *Proc. Roy. Soc.* **162**, 419 (1937).
[12] S. H. HASTINGS, A. T. WATSON, R. B. WILLIAMS and J. A. ANDERSON, JR., *Analyt. Chem.* **24**, 612 (1952).

Treatment of dimethylenetetraborane with methanol should produce the known compound, $(CH_3O)_2BCH_2CH_2B(OCH_3)_2$.[13] The liquid product which was isolated from the reaction shown in equation (1) exerted a vapour pressure of 2 mm at 28·5°. The value reported for the expected product is 1·4 mm at 28·3°.

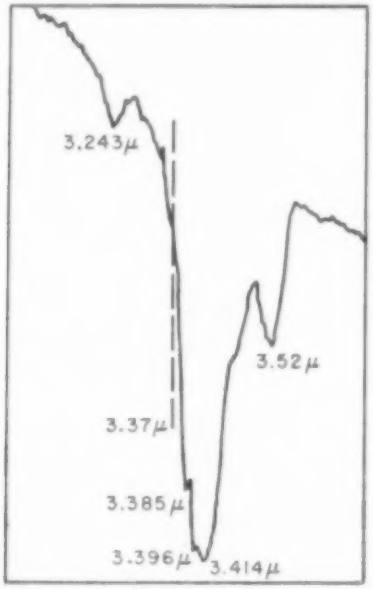

FIG. 3.—Resolved C—H band of dimethylenetetraborane.

All of the evidence obtained appears to support the bridged structure of dimethylenetetraborane.* BURG[15] has studied the reaction of tetraborane and pentaborane-11 with carbon monoxide. A new volatile "polyborine" carbonyl was produced to which the formula B_4H_8CO was assigned on the basis of chemical analysis and molecular weight. The fact that high pressures of carbon monoxide and long reaction times favored the tetraborane reaction would indicate a reaction similar to that of ethylene. While the bond distances and angles of ethane and tetraborane can be used to construct a model of dimethylenetetraborane with no bending of the tetraborane planes, this cannot be done to form a B_4H_8 compound containing a bridging carbonyl linkage. This would not rule out such a structure, but it is also possible that B_4H_8CO is a co-ordination compound similar to borine carbonyl, BH_3CO. The highly unstable B_4H_8 could be formed by the thermal loss of hydrogen from tetraborane or from the symmetrical cleavage of pentaborane-11[16] to yield B_4H_8 and BH_3. The expected BH_3CO was isolated from the pentaborane-11 reaction.

* The nuclear magnetic resonance spectrum of this material recently has been investigated, and the results are consistent with the proposed structure.[14]

[13] G. URRY, J. KERRIGAN, T. D. PARSONS and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **76**, 5299 (1954).
[14] I. SHAPIRO. Private communication.
[15] A. B. BURG and J. R. SPIELMAN, *J. Amer. Chem. Soc.* **81**, 3479 (1959).
[16] L. J. EDWARDS and R. W. PARRY, Paper presented at the 133rd Meeting of the American Chemical Society, San Francisco, California (1958).

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In a study of the thermal decomposition of tetraborane[17] it was necessary to postulate the intermediate formation of B_4H_8 to explain the kinetics. In a study of the exchange between B_2D_6 and tetraborane[18] two rates were observed, the faster one involving two hydrogen atoms of the tetraborane. While it is not necessary that these two reactions proceed by the same mechanism, in the light of the present work and the carbon monoxide work it appears that B_4H_8 is an important structure in the reactions of boranes and that it can be formed by the loss of hydrogen from tetraborane or the loss of BH_3 from pentaborane-11.

Acknowledgement—This work was supported by the Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy, Contract No. NOa (s) 52-1024 (c).

[17] R. J. Pearson and L. J. Edwards, Paper presented at the 132nd Meeting of the American Chemical Society, New York (1957).
[18] J. E. Todd and W. S. Koski, *J. Amer. Chem. Soc.* **81**, 2319 (1959).

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J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 202 to 207. Pergamon Press Ltd. Printed in Northern Ireland

THE REACTION BETWEEN LITHIUM HYDRIDE AND RHODIUM TO FORM A HYDRYL*

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Abstract—The hypothesis is proposed that lithium, rhodium and hydrogen can combine to form a new type of hydrogen compound, a "hydryl" compound. This is analogous to the known carbonyl and cyanyl compounds. The hydride ion, formed by the reaction of lithium and hydrogen, uses its electron pair to enter into co-ordination with rhodium. Some possible reactions are as follows:

$$4Li + Rh + 2H_2 = (Li_4RhH_4)_x$$

$$(Li_4RhH_4)_x + 1/2H_2 = Li_4RhH_5$$

The evidence for these reactions, consisting of powder X-ray diffraction patterns and the stoicheiometry, is given.

The melting points of these "hydryls" appeared to be in the range 565–580°C.

IT has been observed in this Laboratory that when lithium hydride and rhodium metal were heated together to approximately 600°C, a liquid phase appeared. No evolution of gas accompanied this phase change. Since the melting point of lithium hydride is 688°C and rhodium melts at 1966°C, some interaction between the two must have occurred. At room temperature this new phase was a hard, black, crystalline material, virtually opaque. The X-ray diffraction patterns of this product were examined for LiH, LiOH, Li_2O, LiRh, and Rh. None of these was present. Indeed, the complex pattern obtained could not be indexed by powder methods with any certainty. There were indications that the substance might be tetragonal.

EXPERIMENTAL

Materials

Rhodium was obtained from the American Platinum Works. X-ray diffraction patterns of this material gave the literature value for the lattice constant.[1] The lithium (Maywood Chemical Co.) was 99·8 per cent pure according to the manufacturer. For the preparation of lithium hydride this lithium and tank hydrogen, the latter purified by passing over finely divided uranium at 500°C, were heated together. A 347 stainless-steel crucible held the lithium while it was heated to 700°C in an atmosphere of hydrogen. Generally the hydrogen uptake was 98–99 per cent of theoretical. A lithium–rhodium intermetallic phase was made by heating 2·0 mmoles of rhodium with 5·5 mmoles of lithium to 750°C in an argon atmosphere. A soft, malleable alloy resulted.

Apparatus

All the materials were handled and weighed in a dry-box. The air in the box was circulated over alumina to dry it. The reactions were run on a vacuum line. This consisted, aside from the usual necessities of a vacuum system, of a reaction tube (Fig. 1), a standard volume with a mercury

* Work done under the auspices of the Atomic Energy Commission.

[1] G. GOTTFRIED and F. SCHOSSBERGER, *Strukturbericht, Band III*, 1933–1935, p. 182. Edwards Brothers, Ann Arbor, Michigan (1943).

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manometer, and a Toepler pump. The reaction crucible of stainless steel or molybdenum (Fig. 1) could be heated inductively by a 3·5 kW General Electric heater. Temperatures were measured with a calibrated chromel–alumel thermocouple.

The X-ray diffraction patterns were taken on a Norelco diffraction unit using a 114·59 mm diameter powder camera. Copper radiation was used with a nickel filter.

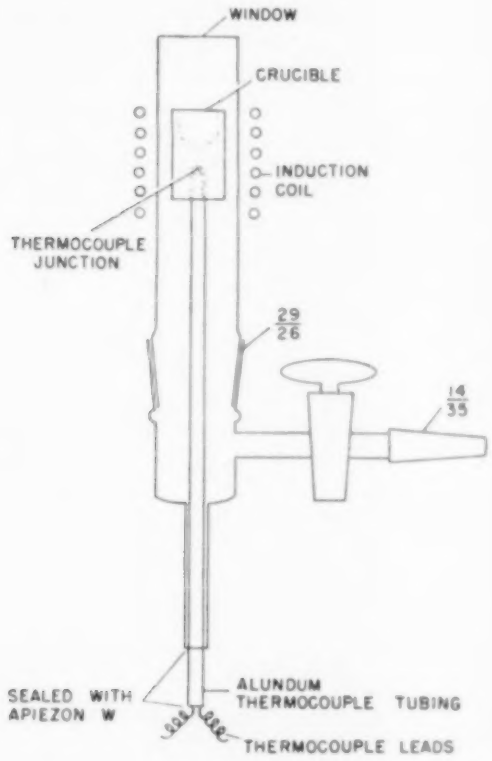

FIG. 1.

Li_4RhH_4

For the preparation of Li_4RhH_4, freshly ground lithium hydride and rhodium powder were heated to 600°C in an argon atmosphere. At approximately 580°C, melting occurred to form a black liquid. The temperature was then held at 600°C for 30 min to promote homogeneity.

Li_4RhH_5

In forming Li_4RhH_5, two alternatives could be followed. Either lithium and rhodium or lithium hydride and rhodium could be heated in hydrogen to 600°C. Again melting occurred at 570–580°C to form a black liquid. This had to be cooled slowly in a hydrogen atmosphere; otherwise varying amounts of hydrogen were taken up. The Li_4RhH_5 dissociated at these temperatures to form Li_4RhH_4 and hydrogen. The hydrogen pressure was kept in the range of 550 mm and by cooling to ~440°C over a period of 1 hr, the hydrogen take-up was reproducible.

Dissociation pressure of Li_4RhH_5

In one experiment, a sample of Li_4RhH_5 was heated in an evacuated closed system and the pressure was measured as a function of temperature. The pressure was followed with rising temperature only, as an air leak developed and terminated the experiment. The pressure appeared to reach a

steady value slowly. For instance, after three days at 435°C, the pressure still seemed to be rising slowly. This could have been due to the slow distillation of lithium metal from the sample. A deposit was visible on the walls of the apparatus around the sample crucible.

RESULTS

Several solvents were tried on these hydryls in an attempt at purification. With pyridine and n-propyl amine, a dark colour formed in the liquid, but very little solid dissolved. Both water and alcohol caused decomposition with evolution of hydrogen and re-formation of Rh. Since there appeared to be no easy way to purify the hydryl and thus get its composition, the starting materials had to be varied in their proportions to see what effect this would have on the product. Free rhodium could be detected in a preparation by means of X-ray patterns, but free lithium hydride would in general be masked owing to the large difference in density. In the case of Li_4RhH_5 preparations, the amount of hydrogen uptake would give an indication of the amount of rhodium reacting. The data obtained by varying the composition of the starting material are given in Table 1 for Li_4RhH_5. The mole fractions used (Table 1) were calculated on

TABLE 1.—COMPOSITION VS. X-RAY RESULTS

N_{Li}	$\frac{H}{Li}$	$\frac{H^*}{Rh}$	Rh from X-ray
0·67	1·25	0·51	*s*
0·80	1·25	0·99	*w*
0·80	1·25	1·00	*w*
0·81	1·22	0·90	*nd*
0·85	1·16	0·94	*np*
0·91	1·09	0·93	*w-*
0·96	1·05	1·02	*nd*

s = strong; *w* = weak; *nd* = not detected; *np* = no pattern taken.

the basis of lithium and rhodium as the only components, with hydrogen omitted for simplicity. The ratio H/Li gives the total number of hydrogen atoms which reacted in a preparation divided by the number of lithium atoms present. In the next column the H* represents the total number of hydrogen atoms reacting minus the number theoretically required to react with the lithium present to form lithium hydride. In other words, it represents the excess hydrogen which was available for the rhodium.

It can be seen from the table that in a preparation carried out in hydrogen when the mole fraction of lithium was 0·67, the ratio H/Li was 1·25 and free rhodium was present. Upon increasing N_{Li} to 0·8, the value of 1·25 persisted for H/Li and little free rhodium was detected. The H*/Rh value also increased to approximately one. Further increase in lithium content caused the H/Li ratio to decrease while H/Rh remained roughly one, the free rhodium disappearing simultaneously. Visually, it could be seen that the sample with N_{Li} equal to 0·91 contained two phases, one a clear colourless material, the other, black. The clear material was optically isotropic with a refractive index between 1·8 and 2·1†. Presumably, the clear material was lithium hydride. These results were interpreted as follows. At N_{Li} equal to 0·67, the phases present were Li_4RhH_5, and Rh. Consequently the ratio H/Li should be 1·25. The

† Microscopy performed by E. STARITZKY of this laboratory.

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H*/Rh ratio would be a variable here. Upon increasing the lithium content, more Li_4RhH_5 formed until at N_{Li} equal to 0·8 the stoicheiometry would be that of Li_4RhH_5. Further increase in lithium content resulted in the formation of LiH and Li_4RhH_5. In this case the H/Li ratio should decrease while H*/Rh should remain one.

Upon heating the Li_4RhH_5, hydrogen was evolved reversibly. Some very approximate measurements of the dissociation pressure are in Table 2. From visual

TABLE 2.—DISSOCIATION PRESSURE AS A FUNCTION OF TEMPERATURE

Temperature (°C)	Pressure (mm)
286	6·5
380	34·0
425	48·0
435	80·0

observations and the X-ray diffraction patterns, it was concluded that there was little or no solid solubility of LiH, Li_4RhH_4 and Li_4RhH_5 in one another. Consequently the following reaction was assumed for the dissociation:

$$2\ Li_4RhH_5 = (Li_4RhH_4)_2 + H_2.$$

The pressure data were plotted and a line drawn through as well as possible. This gave the equation:

$$\log P = \frac{-2900}{T} + 6{\cdot}00$$

from which the heat of dissociation was calculated to be approximately 13 kcal/mole hydrogen.

A solid composition approximating Li_4RhH_4 was prepared by heating lithium hydride and rhodium in an argon atmosphere. The same material also resulted when Li_4RhH_5 was heated to 400°C in vacuum and the gas pumped off with a Toepler pump. Hydrogen evolution stopped when the solid composition reached Li_4RhH_4. The X-ray diffraction pattern contained neither rhodium nor lithium hydride lines. Also the pattern differed from that of Li_4RhH_5. The patterns obtained are shown in Table 3. There appears to be indications of a tetragonal structure in each. However, the patterns were considered too complicated to resolve by powder methods.

On the chance that a lithium–rhodium intermetallic compound might be present in some of the preparations, an X-ray pattern was taken of a material made by heating lithium and rhodium. This pattern is also shown in Table 3 as indexed by F. ELLINGER. It was never found in any of the Li_4RhH_4 or Li_4RhH_5 patterns. The material is simple hexagonal with $a_0 = 2{\cdot}66$ Å and $c_0 = 4{\cdot}35$ Å.

The observed melting points of Li_4RhH_4 and Li_4RhH_5 varied between 565–580°C. This variation could be due to two factors: (1) it takes only a small amount of lithium hydride weight-wise to give an appreciable mole fraction; (2) the Li_4RhH_5 can dissociate to Li_4RhH_4. The figure 565°C may be eutectic temperature with lithium hydride. The extent of the dissociation of Li_4RhH_5 at temperatures around 565°C was not realized until the work was nearly ended. The observed dissociation pressure at this temperature was 340 mm, while melting points were taken with anywhere

from 100 to 400 mm pressure of hydrogen. In general, it seemed as if the Li_4RhH_5 must have a lower melting point than Li_4RhH_4, since during the course of a heating of this, there would first be melting, then an evolution of gas as evidenced by bubbles forming in the melt, and finally some solid would appear in the melt before it all became liquid again.

TABLE 3.—*d* VALUES OBSERVED

Li_4RhH_5		Li_4RhH_4		Li–Rh	
Intensity	*d*	Intensity	*d*	Intensity	*d*
s	4·43	*s*	4·44	*s*	4·34
m	3·98	*w*—	3·54	*s*—	2·29
w—	3·63	*s*	3·44	*w*—	2·17
w—	3·52	*w*—	3·28	*s*—	2·03
w	3·39	*m*—	3·14	*m*	1·57
s—	3·28	*s*	2·32	*w*—	1·44
m—	3·14	*w*—	2·22	*w*—	1·32
w— —	2·76	*w*—	2·05	*w*—	1·26
w	2·46	*w*	1·99	*w*	1·22
w +	2·36	*w*	1·86	*w*—	1·15
m	2·26	*w*	1·72	*w*	1·13
w— —	2·21	*w*—	1·61	*w*—	1·11
w	2·08	*w*	1·51	*w*—	1·08
w—	1·99	*w*—	1·49	*w*—	1·01
w—	1·93	*w*—	1·43	*w*	0·981
w	1·84	*m*—	1·41	*w*—	0·900
w	1·78	*w*— —	1·25	*w*—	0·871
w—	1·64	*w*—	1·23	*w*	0·850
w—	1·62	*w*	1·21	*w*	0·841
w—	1·58	*w*—	1·16	*m*	0·815
w—	1·53	*w*— —	1·13	*w*	0·813
w—	1·47	*w*— —	1·08	*m*—	0·808
w—	1·39	*w*— —	1·06	*w*	0·804
w	1·31	*w*—	0·96	*m*	0·790
w— —	1·25	*w*—	0·93	*w*	0·788
w— —	1·22	*w*— —	0·923		
w—	1·19				
w	1·17				

s = strong; *m* = medium; *w* = weak.

The formulae Li_4RhH_5 and Li_4RhH_4 appeared to be indicated by the stoicheiometry of the reactants. They could also be drawn by analogy to the known rhodium carbonyls and carbonyl hydride.[2] For instance, the following reaction is known

$$2Rh(CO)_4H = [Rh(CO)_4]_2 + H_2$$

By substituting H^- for CO one gets the hydryl. The Li^+, of course, must also be added for neutrality. In addition to the two above carbonyl compounds there are also known $[Rh(CO)_3]_x$ and $[Rh_4(CO)_{11}]_x$. It is therefore possible that more hydryls exist and that a mixture was obtained. More careful work would have to be done to resolve this.

[2] H. J. EMELEUS and J. S. ANDERSON, *Modern Aspects of Inorganic Chemistry* (2nd Ed.) p. 408. Van Nostrand, New York (1952).

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Another compound that can be drawn upon for an analogy is $K_4Ni(CN)_4$, a cyanyl.[3] This is a compound of zero-valent nickel. It can be considered as derived from $Ni(CO)_4$ by the replacement of the CO by $(CN)^-$. Palladium also forms a compound of this type, namely $K_4Pd(CN)_4$.

CONCLUSION

Evidence has been presented for the possible existence of a new class of hydrogen compounds. They are considered as derived from known rhodium carbonyls by replacing the (CO) with $(H)^-$. That it is possible to replace the neutral (CO) by the charged $(CN)^-$ has been demonstrated by other workers in the case of nickel. The resulting compound was termed a cyanyl; hence it was felt that hydryl would be an appropriate name. It would be desirable to have more evidence of the existence of these hydryls. For instance, single-crystal X-ray work might resolve the structure and give the Rh–Rh distance. Also, magnetic susceptibility measurements might indicate the type of bonding, if any, between rhodium and hydrogen.

Acknowledgements—The author wishes to thank M. G. BOWMAN, F. H. ELLINGER and D. T. VIER for many helpful discussions.

[3] J. EASTES and W. BURGESS, *J. Amer. Chem. Soc.* **64**, 1187 (1942).

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PREPARATION AND PROPERTIES OF HIGH PURITY YTTRIUM METAL*

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Abstract—Yttrium metal in 99·8 per cent purity was prepared by lithium reduction of anhydrous yttrium chloride prepared from commercial yttrium oxide. Physical properties of the metal so prepared are given and analytical procedures for its evaluation are discussed.

PURE yttrium metal has been difficult to prepare because of its electropositive character as well as its similarity to, occurrence with, and difficulty of separation from the lanthanide elements. As a result considerable variation in chemical, physical and metallurgical properties of yttrium have been reported. Ion exchange techniques[1,2] have made available a source of pure yttrium salts for the preparation of the pure metal so that its properties may be more correctly evaluated. In addition, recent data[3] has indicated that yttrium may have nuclear and metallurgical applications. For these reasons the production of pure yttrium metal in massive form is of current interest.

The most successful metallothermic preparations of massive yttrium are those of DAANE and SPEDDING[4], and CARLSON *et al.*[5] Essentially these methods involve the reduction of yttrium fluoride with calcium to form the molten metal directly, the reduction of an yttrium fluoride–zinc fluoride mixture with calcium to form an intermediate zinc alloy of yttrium or the reduction of an yttrium fluoride-calcium chloride mixture with metallic calcium and magnesium to form an yttrium–magnesium alloy.

Yttrium metal available to the authors at the time this investigation was made was prepared by the magnesium intermediate alloy method of CARLSON *et al.* This metal was of production grade quality and had a relatively high oxygen contamination and has been observed to contain varying amounts of non-metallic inclusion phases in its microstructure. These impurities are believed to be responsible for the variation in chemical, physical and metallurgical properties observed on yttrium metal produced by this method.

Electrolytic preparation of massive yttrium metal has not been very successful. The only significant method has been reported by TROMBE and MAHN[6] in 1945. These investigators prepared a cadmium–magnesium–yttrium alloy by electrolysis of a fused salt bath of sodium chloride using a cadmium–magnesium anode.

* This paper represents a part of the dissertation submitted by H. J. NOLTING to the Graduate School of Xavier University in partial fulfillment of the requirement for the degree of Master of Science.

(1) F. H. SPEDDING *et al. J. Amer. Chem. Soc.* **70**, 1671 (1948).
(2) F. H. SPEDDING, *Chem. Engng. News* **30**, 1200 (1952).
(3) R. B. HOWES, *Metal Progr.* **75**, No. 6, 108 (1959).
(4) A. H. DAANE and F. H. SPEDDING, *J. Electrochem. Soc.* **100**, 442 (1953).
(5) O. N. CARLSON, F. A. SCHMIDT and F. H. SPEDDING, U.S.A.E.C., ISC-744 (1956).
(6) F. TROMBE and F. MAHN, *C. R. Acad. Sci., Paris* **220**, 778 (1945).

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This investigation describes the direct preparation of pure yttrium metal from yttrium chloride starting with yttrium oxide. Lithium is used as the reducing agent because the lithium chloride by-product can be removed from the yttrium metal by distillation at reasonably low temperatures. The procedure is as follows:

$$Y_2O_3 + 6HCl + 3H_2O \longrightarrow 2YCl_3 \cdot 6H_2O \quad (1)$$

$$YCl_3 \cdot 6H_2O + HCl\,(gas) \xrightarrow[1\cdot2\text{-}1\cdot3\ atm]{110^\circ C} YCl_3 \cdot H_2O + H_2O\,(gas) \quad (2)$$

$$YCl_3 \cdot H_2O + x HCl\,(gas) \xrightarrow[1\cdot2\text{-}1\cdot3\ atm]{110\text{-}350^\circ C} YCl_3 \cdot x HCl + H_2O\,(gas) \quad (3)$$

$$YCl_3 \cdot x HCl \xrightarrow[Pt\ Cruc.\text{-}He\ gas]{1000^\circ C} YCl_3\,(crude) + HCl\,(gas) \quad (4)$$

$$YCl_3\,(crude) \xrightarrow[950^\circ C\text{-}0\cdot05\ mm]{distilled} YCl_3\,(purified) \quad (5)$$

$$YCl_3\,(purif.) + 3Li\,(gas) \xrightarrow[Ta\ Cruc.]{950^\circ C} Y - 3LiCl\,(mixture) \quad (6)$$

$$Y - 3LiCl\,(mixture) \xrightarrow[Ta\ Cruc.]{1000^\circ C} Y\,(crystal) + 3LiCl\,(gas) \quad (7)$$

EXPERIMENTAL

Preparation of yttrium chloride hexahydrate[7]

Yttrium chloride was prepared by digesting yttrium oxide (Ames Laboratory, Iowa State College—see Table 1) in concentrated hydrochloric acid, evaporation of solvent until crystallization occurred and vacuum drying of the crystals at 90 C for 1 hr. (Yttrium, 29·08; Theor. 29·64; Chlorine, 34·75; Theor. 35·06; Water 36·17 by diff., theor. 35·30%)

TABLE 1.—SPECTROGRAPHIC ANALYSIS OF YTTRIUM OXIDE*

Element	Contents (p.p.m.)	Element	Contents (p.p.m.)
Aluminum	1	Lutetium	<2
Barium	<1	Magnesium	15
Bismuth	3	Manganese	4
Boron	1	Nickel	100
Cadmium	<30	Niobium	30
Calcium	<6	Potassium	<1
Chromium	100	Samarium	<3
Cobalt	1	Silicon	100
Copper	5	Sodium	10
Dysprosium	<1	Tantalum	60
Europium	<3	Terbium	<2
Gadolinium	<2	Titanium	<3
Iron	10	Vanadium	1
Lead	<15	Zinc	3
Lithium	<1	Zirconium	3

Total volatile material . . . 0·7 weight per cent
Total rare earth—by difference . . . 99·25 weight per cent

* Spectrographic analysis by the General Electric Aircraft Nuclear Propulsion Department, Cincinnati Ohio.

[7] J. A. KLEINHECKSEL and H. C. KREMERS, *J. Amer. Chem. Soc.* **50**, 959 (1928).

Preparation of anhydrous yttrium chloride

Yttrium chloride hexahydrate was dehydrated by passing anhydrous hydrogen chloride gas (Matheson Company, Inc., East Rutherford, N.J.) under a slight positive pressure downward through a dehydrating tower (Matheson Company, Inc., East Rutherford, N.J.—see Fig. 1) containing the yttrium chloride at carefully controlled temperatures. A mercury column was used to control the pressure and monitor the rate of flow. Starting at 110°C approximately 0·5 l/min of hydrogen chloride was passed through the column for 24 hr by which time no increase in water was noted

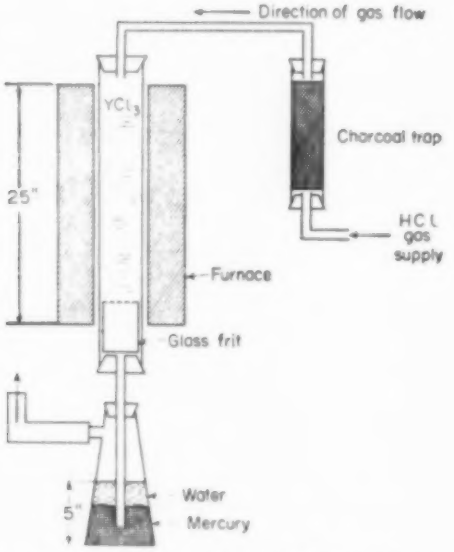

FIG. 1.—Yttrium chloride hexahydrate dehydration apparatus.

above the mercury column (see Fig. 1). The amount of water corresponded to about 80 per cent of the water of hydration of the yttrium salt. The temperature was then raised to 350°C for twenty-four additional hours. The system was cooled, the dehydrated yttrium chloride removed from the tower, melted in a platinum crucible at 1000°C in an inert atmosphere to remove hydrogen chloride and cast into rods of approximately 100 g (1 in. diameter by 3 in. long) using a copper mould. Quantitative yields were obtained.

Purification of anhydrous yttrium chloride

Apparatus. A distillation retort was constructed from 0·035 in. thick platinum sheet. Basically this retort was a crucible 2½ in. diameter by 11½ in. high. At a distance of 6 in. from the bottom an inner trough was so constructed that it was slightly oblique to the horizontal plane of the crucible. At the lowest point of the trough, a platinum spout was welded through the wall to allow drainage of molten salt into a copper mould. This spout was tubular in form, ⅜ in. diameter having a bore of approximately ¼ in. and extending 2½ in. down and away from the side of the crucible wall. The tip was slightly flared to facilitate drainage of the distilled molten salt. The receiving mould was of annealed copper measuring 1½ in. internal diameter and 3½ in. deep.

To achieve the conditions of vacuum and temperature necessary for the distillation, a NRC model 2904B vacuum casting unit, manufactured by the NRC Equipment Corporation of Newton Highlands, Massachusetts, was used. Slight modifications of the vacuum chamber were made to accommodate the distillation retort and copper receiving mould. Fig. 2 shows the complete assembly prior to a distillation.

Procedure. The anhydrous yttrium chloride was purified by vacuum distillation. Distillations were conducted on 100 g crude yttrium chloride rods. A temperature of 1000°C under a vacuum of 100 μ or less was found to give a distillation rate of 5–6 g/min. The colourless chloride condensed on

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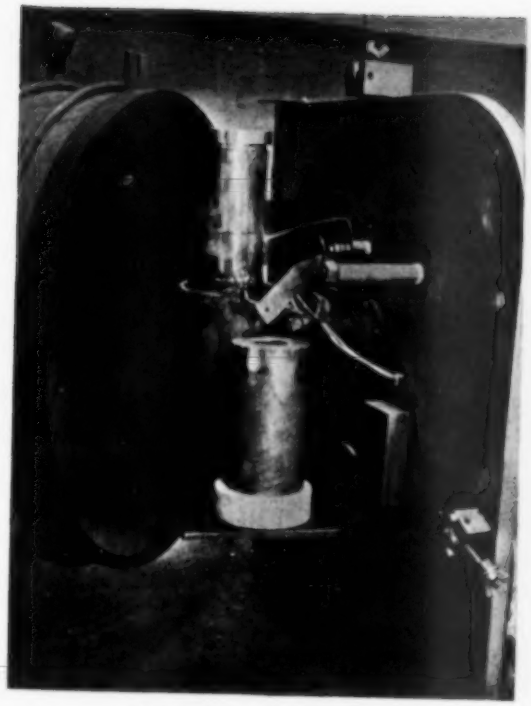

FIG. 2.—Distillation apparatus.
Note copper mould in foreground with drip-spout positioned directly above. Platinum retort is heated by a molybdenum element (not shown) surrounded by the outer cooling jacket.

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the interior upper walls of the distilling retort, collected in the trough and then dripped from the distillation retort sidespout into the copper receiving mould. Approximately 150–160 g of fused yttrium chloride salt was recovered per distillation in the form of a billet. This represented yields of 75–80 weight per cent. The billets were then distilled a second time to insure maximum purity, the final product being a clear crystalline billet of the fused salt measuring 1½ in. diameter by approximately 3 in. long and weighing 150–160 g.

Evaluation. Analysis of distilled yttrium chloride was limited since sampling procedures called for the destruction of a billet and subsequent time consuming recasting and redistillation. The chloride prepared after the second distillation appeared completely soluble in water. (Yttrium chloride is soluble in water, yttrium oxide and yttrium oxychloride are not.) However, to substantiate the effect of distillation, nominal oxygen analyses were made on the raw yttrium chloride and the products of small scale first and second distillations. A neutron activation method[8] was used to determine the amount of oxygen in the yttrium chloride. Residues in the retort were analysed by X-ray diffraction methods. In two residue samples each from a first and second distillation, yttrium oxychloride was identified as the major phase. The cell structure of this compound was reported to be tetragonal with a unit cell volume of about 100·58 Å^3. The cell dimensions were reported as: a_0 = 3·91 Å; c_0 = 6·58 Å; c_0/a_0 = 1·68. Traces of a minor phase were observed but not identified.

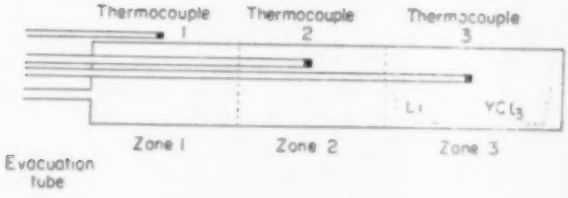
Reduction of yttrium chloride to yttrium metal

Materials. The following materials were used in the reduction process:

1. Yttrium chloride billets weighing 150–160 g prepared as described.
2. Lithium metal purchased from the American Potash and Chemical Company of America. This metal was received in the form of 100–200 g ingots packed in argon. The chemical purity was reported as follows: Li, 99·97; Na, 0·0009; Ca, 0·15 per cent by weight.
3. Type 310 stainless steel pipe and plate. The pipe had an inside diameter of 3 in. and ¼ in. wall thickness. The plate was ¼ in. thick. Tubing was heavy-walled having an outside diameter of ¼ in.
4. Tantalum sheet, 0·020 in. thick and unannealed molybdenum sheet, 0·010 in. thick, purchased from the Fansteel Metallurgical Corporation, N. Chicago, Illinois.
5. Titanium foil, 0·005 in. thick purchased from the Titanium Metals Corporation of America, New York City, New York.

Apparatus. The reduction crucibles were formed from the 0·020 in. tantalum sheet by folding into rectangular boxes measuring 2¼ in. by 2¼ in. by 4 in. long.

The bombs used were constructed entirely from Type 310 stainless steel pipe, plate and tubing. The bomb proper was made of 3 in. pipe, cylindrical in shape and 22 in. long. Closure was accomplished by welding a ¼ in. thick circular plate into one end and a similar plate into the other end, this plate having a heavy-walled ¼ in. evacuation tube. The length of the evacuation tube was 4 ft. The bomb was then arbitrarily divided into three zones: Zone 1 extending from the face plate of the bomb to a length of 7 in.; Zone 2 extending from 7 to 14 in.; and Zone 3 extending from 14 to 22 in. (See Fig. 3). Thermocouples were centrally placed in each zone to monitor temperature differential.



Total Length	22	inches
Zone 1	7	inches
Zone 2	7	inches
Zone 3	8	inches

FIG. 3.- Reduction bomb assembly.

[8] G. M. LEDICOTTE, Oak Ridge National Laboratory. Private communication. September (1958).

Two 4 in. tantalum boats containing respectively lithium and yttrium chloride were placed in Zone 3 prior to closure of the bomb chamber. The face plates and bomb chamber were cleaned with hydrochloric acid, rinsed with deionized water and air dried before assembly. Fig. 3 schematically represents the assembled bomb as used for all reductions.

A Leeds and Northrup Model 8657–C potentiometer was used to measure the temperature.

A Harper furnace Model HOV-10618-M-26 with a maximum operating temperature of 1500°C over a zone 6 in. square and 24 in. in length was used as the reduction furnace.

A Welch Duo-Seal vacuum pump Model 1397 was used to evacuate the bomb chamber.

Procedure. A total of three reductions were made.

Reduction 1—Two yttrium chloride billets with a total weight of 315 g and a block of clean lithium weighing 40 g were placed in their respective containers and positioned in Zone 3 of the bomb chamber. The face plate was welded into position and a vacuum immediately drawn on the bomb chamber. When a vacuum of 50 μ or less had been achieved, the reduction schedule was initiated by placing the evacuated bomb in the preheated reduction furnace in a horizontal position. A temperature of 950°C was attained in 15 min and held for 2 hr over the entire length of the bomb. Vacuum readings indicated the evacuation tube was sealed within the first 5 min exposure to temperature. Closure was due to condensation of lithium vapour in the evacuation tube which sealed the bomb and its contents during the reduction. After 2 hr the bomb was positioned so that the face plate extended slightly from the furnace opening. An air blast was directed at the face plate. The furnace temperature was raised so that within 30 min a steady temperature of 1000°C on Zone 3, 950°C on Zone 2 and 400–500°C on Zone 1 were recorded. This temperature gradient was maintained for 12 hr. After this period the bomb was removed from the furnace and cooled. The bomb chamber was cut open in Zone 2 at the thermocouple position and argon gas was flushed into the chamber immediately after an opening was made. The gross appearance and position of the reduction products appeared to be as expected. However, the yttrium had overflowed one section of the reduction crucible and reacted slightly with the chamber wall. The crucible adhered to the wall at this point and when attempts were made to pry it loose spontaneous ignition occurred and spread to the whole container. The yttrium metal burned with an intense greenish-white light and gave off considerable heat. All of the product was lost.

Reduction 2—To prevent another loss of product the bomb was lined with 0·010 in. molybdenum foil before assembly. The reduction crucibles were also placed on a tantalum tray constructed from 0·020 in. sheet and the crucibles themselves were shaped to better conform with the chamber geometry. Two billets of yttrium chloride weighing 300 g and 40 g of lithium were used. The reduction schedule was carried out exactly as in Reduction (1). Removal of the reduction crucible was accomplished successfully and approximately 130–140 g of crystalline yttrium was recovered. This was present in a sponge-like form completely contained within the tantalum crucible. The extreme top portion of the sponge was slightly darkened; this was mechanically separated from the main portion. About 110 g of crystalline yttrium remained.

Reduction 3—Two billets of fused yttrium chloride weighing 305 g and 40 g of lithium were used. Assembly of the reduction apparatus was the same as in Reduction (2) with the exception that 0·005 in. titanium foil as an addition liner was used as a getter for gaseous contaminants. The reduction schedule was also the same and approximately 125 g of bright crystalline yttrium sponge was recovered.

TABLE 2.—ANALYTICAL EVALUATION OF ANHYDROUS YTTRIUM CHLORIDE

	Raw cast YCl_3	Distilled YCl_3	Redistilled YCl_3
Solubility in water	—	—	—
Oxygen (weight per cent) (neutron activation)	1·10 ± 0·02	0·83 ± 0·16	0·35 ± 0·05
Chloride (weight per cent) (Mohr) (Theoretical — 54·47)	—	53·04	54·14
Yttrium (weight per cent) (Oxalate) (Theoretical — 45·53)	—	45·35	45·06
Residue as YOCl (weight per cent)	—	2·40	0–0·5

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There was no discoloration of this sponge although some of the crystals adhered to the tantalum crucible. Fig. 4 shows some typical crystals obtained by this reduction.

Evaluation. For a comparative analysis arc-melted buttons weighing approximately 10 g were prepared from the crystals obtained from Reductions (2) and (3). The vacuum fusion method was used to determine oxygen and nitrogen and the bromine insoluble method[49] used to determine total non-metallic content of the metal. Theoretically, this latter analysis determines the total amount of non-metallic impurities in yttrium metal. The procedure, which is under development, is as follows:

Approximately 1 g of yttrium metal is placed in 120 ml of anhydrous methanol. Small portions of bromine are added to this until all the yttrium metal dissolves, then a small excess of bromine is added. Another 100 ml of methanol is added and this solution is filtered. Any residue is dried at 110 C for 30 min. This residue is considered the total non-metallic residue from the sample and the purity is calculated accordingly.

TABLE 3.—ANALYTICAL EVALUATION OF CHLORIDE REDUCED YTTRIUM METAL

	Reduction (2)	Reduction (3)
Oxygen (weight per cent) (Vacuum fusion)	0·313	0·162
Nitrogen (weight per cent) (Vacuum fusion)	0·024	0·006
Bromine Insoluble (weight per cent) (Non-metallic impurities)	0·28	0·17
Carbon (p.p.m.) (Combustion)		70
Chloride (p.p.m.) (Conductometric)		100
Yttrium (weight per cent) (Oxalate)		99·91

Table 3 lists the results of the analyses performed. A spectrographic analysis of the arc-melted specimen from Reduction (3) is listed in Table 4. Microstructures of specimens prepared by this procedure were exceptionally clean as compared to the usual yttrium metal prepared by a fluoride reduction. Figs. 5 and 6 illustrate this point. No intergranular inclusions were detected at magnifications as high as 750 . .

Properties of high purity yttrium metal

Some properties of the yttrium metal prepared by lithium reduction of yttrium chloride were determined and compared with similar properties which had been determined on metal prepared through the intermediate alloy process. Table 5 lists these properties. The crystal structure, lattice parameters, axial ratio and crystal density of chloride reduced metal were obtained from X-ray diffraction powder patterns. Filings were taken from an arc-melted button of the metal and were annealed at 1350 C for 1 hr. The patterns were obtained using a Norelco 114·6 mm diameter powder camera. Powder patterns obtained are given in Table 6. Crystallographic data obtained by HERMANN *et al.*[50] on yttrium metal purified by vacuum distillation are also given in Table 5. In this study, the diffraction pattern was obtained on a sample of yttrium metal which had been distilled from tantalum and condensed on a tantalum surface.

The measured densities of both chloride reduced and intermediate alloy yttrium metal were obtained by a displacement method in which arc-melted buttons of the metal were weighed in air and then in toluene.

The melting point of chloride reduced yttrium was determined by melting a portion of the primary crystalline product and observing the characteristics of the cooling curve obtained from e.m.f. measurements using a rhenium–tungsten thermocouple. The metal was melted in a tantalum crucible

[49] R. A. DUNLEAVY, General Electric Aircraft Nuclear Propulsion Department, Cincinnati, Ohio. Unpublished work (1958).
[50] K. W. HERMANN, A. H. DAANE and F. H. SPEDDING, U.S.A.E.C., ISC-702 (1955).

TABLE 4.—SPECTROGRAPHIC ANALYSIS OF ARC-MELTED YTTRIUM METAL PREPARED BY CHLORIDE REDUCTION

Element	Contents (p.p.m.)	Element	Contents (p.p.m.)
Aluminum	30	Lutetium	<5
Barium	<1	Magnesium	5
Bismuth	30	Manganese	20
Boron	10	Nickel	10
Cadmium	<30	Niobium	30
Calcium	10	Potassium	<1
Chromium	30	Samarium	<5
Cobalt	1	Silicon	200
Copper	20	Sodium	3
Dysprosium	<2	Tantalum	60
Europium	<5	Terbium	<2
Gadolinium	<2	Titanium	<3
Iron	100	Vanadium	3
Lead	<20	Zinc	3
Lithium	<1	Zirconium	30

Total non-metallic content . . . 0·17 weight per cent
Total rare earth content—oxalate method . . . 99·91 weight per cent

TABLE 5.—PROPERTIES OF YTTRIUM METAL

	Chloride reduced metal	Intermediate alloy* metal
Crystal structure†	*hcp*	*hcp*
Lattice parameter,† a_0 (Å)	3·648	3·649
c_0 (Å)	5·737	5·737
Axial ratio,† c_0/a_0	1·573	1·572
Crystal density,† D_x, 25°C, (g/cm³)	4·466	4·464
Measured density,† p, 25°C, (g/cm³)	4·45	4·4–4·6
Melting point,† °C	1525 ± 10°C	1540 ± 10°C
Transition temperature (°C)	(1472 ± 10)	—
Elec. resistance, 25°C, ($\mu\Omega$cm)	74·1	69–70
Ultimate strength, 25°C, (lb/in² × 10³)	20·9	24·2
Yield strength, 25°C, 0·2% offset, (lb/in² × 10³)	16·9	13·8
Tensile elongation, 25°C, (%)	11·0	7·0
Coefficient of linear thermal expansion, $\alpha \times 10^6$		
25–300°C	7·6	9·3
25–600°C	9·3	10·9
25–900°C	9·9	11·3
25–1000°C	10·1	11·6
Arc-melt Brinell Hardness (500 kg load, 10 mm ball)	45–50	65–75

* Property values given for intermediate alloy metal are representative of those measured during this study on a metal averaging 2500 p.p.m. in oxygen content and total rare earth of 99·3 per cent by weight.
† HERRMANN *et al.* obtained the following values on yttrium metal purified by vacuum distillation

Lattice parameter, a_0Å	3·6474 ± 0·0007
c_0Å	5·7306 ± 0·0008
Axial ratio, c_0/a_0	1·571
Crystal density, D_x, 25°C, (g/cm³)	4·472
Melting point (°C)	1550 ± 5

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FIG. 4—Crystalline yttrium obtained from reduction of yttrium chloride with lithium. Note hexagonal structure of crystals. (10×).

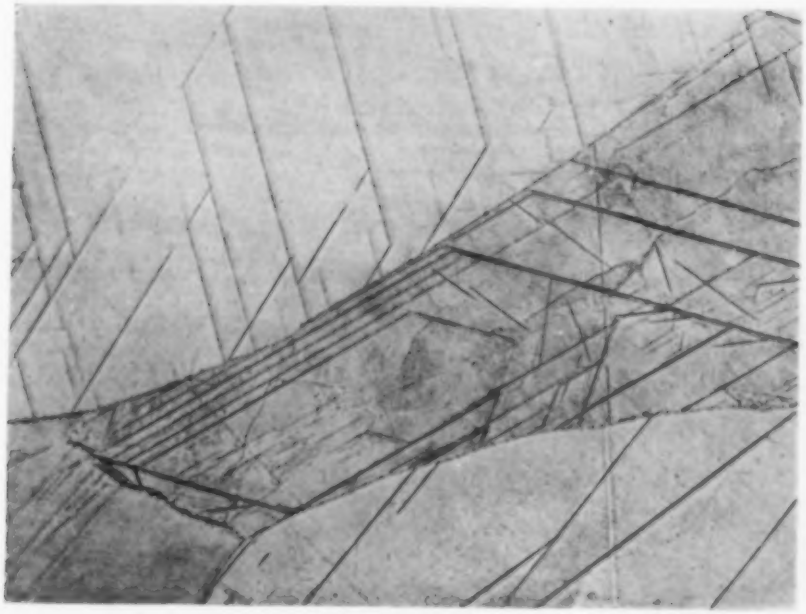

FIG. 5.—Photomicrograph of yttrium metal produced by reduction of yttrium chloride with lithium. Note excessive twinning. HNO_3 Etch. (250×).

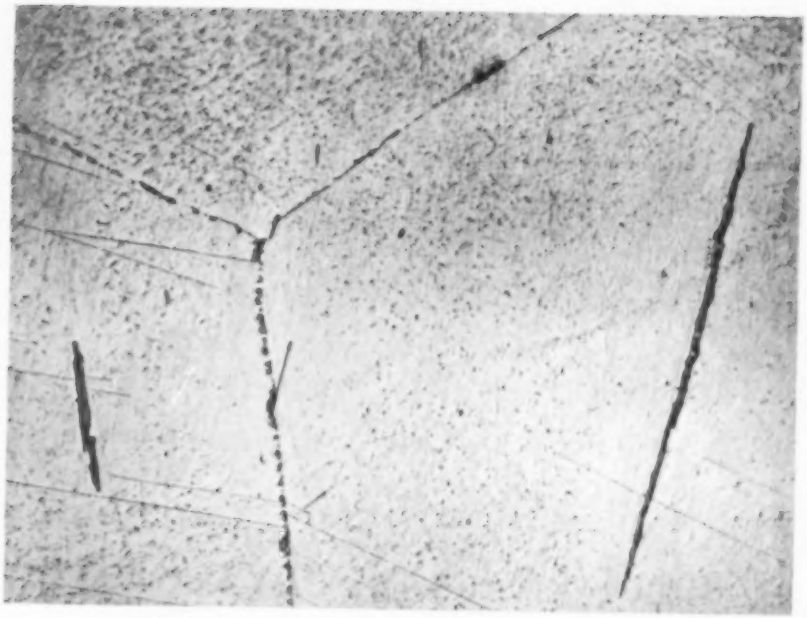

FIG. 6.—Photomicrograph of yttrium metal currently available from the magnesium-intermediate alloy process. Fine scattering of dark impurity phases present within grains and at grain boundaries. HNO_3 Etch. (250 ×).

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TABLE 6.—X-RAY DIFFRACTION PATTERN OF YTTRIUM METAL[10]

Diffraction pattern of intermediate alloy and chloride reduced metal

d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
3·158	*s*	100	1·054	*w*	300
2·869	*s*	002	1·013	*m*	213
2·768	*vs*	101	0·9888	*mw*	302
2·124	*ms*	102	0·9566	*vvw*	006
1·823	*ms*	110	0·9286	*w*	205
1·635	*ms*	103	0·9180	*vw*	214
1·579	*w*	200	0·9123	*vw*	220
1·539	*ms*	112	0·8768	*vvw*	310
1·523	*m*	201	0·8696	*w*	222
1·433	*w*	004	0·8668	*mw*	311
1·384	*mw*	202	0·8492	*vw*	304
1·306	*w*	104	0·8473	*w*	116
1·217	*mw*	203	0·8385	*vvw*	312
1·194	*vw*	210	0·8278	*mw*	215
1·169	*m*	211	0·8184	*vvw*	206
1·127	*mw*	114	0·7969	*mw*	313
1·103	*w*	212	0·7938	*vw*	107
1·079	*mw*	105	0·7829	*w*	401
1·062	*vw*	204			

Hexagonal unit-cell dimensions

Intermediate alloy		Chloride reduced	
a	3·649 Å	a	3·648 Å
c	5·737 Å	c	5·737 Å
c/a	1·572	c/a	1·573
Vol.	66·154 Å³	Vol.	66·121 Å³
D_x	4·464	D_x	4·466

under one atmosphere helium gas pressure. The thermocouple was inserted into a thin-walled molybdenum tube, closed at the bottom and immersed in the molten metal. Temperature control was maintained by means of a Minneapolis–Honeywell Brown Rubicon potentiometer. An inflexion was observed in the cooling curve at temperatures slightly below the melting point. Although not as yet confirmed by high temperature X-ray diffraction patterns, the inflexion indicates that a high temperature crystalline modification exists whose transition temperature is roughly in the range given in Table 5. The melting point of a representative sample of the arc-cast intermediate alloy metal was determined by the same method. Unpublished studies of the Y–Mg, Y–La and Y–Th alloy systems indicate that a body-centred cubic modification of yttrium exists with an estimated transition temperature somewhere above 1450°C.[11,12]

Specimens of both types of metal were rolled into 0·040 in. thick sheet which were then cut into 2 in. lengths, 0·250 in. wide. These specimens were then used to determine the electrical resistivity of yttrium at room temperature. The measurements were obtained by determining the ratio of the potential drop across a standard resistor (0·1 Ω) and a measured length of specimen, both of which

[11] F. D. GIBSON and O. N. CARLSON, ASM Preprint No. 146; To be published in *Trans. Amer. Soc. Metals* **52**, (1959).

[12] D. T. EASH and O. N. CARLSON, ASM Preprint No. 142; To be published in *Trans. Amer. Soc. Metals* **52**, (1959).

[13] R. C. RAU, General Electric Aircraft Nuclear Propulsion Department, Cincinnati, Ohio. Unpublished work (1959).

were connected in series to a 6 V battery and a variable resistor. Current leads and potential leads were of copper spot-welded to the ends and gauge marks of the yttrium specimens. The potential drop across both standard resistor and specimen were measured by means of a Leeds and Northrup potentiometer No. 751314.

Short time tensile strengths were determined on button-head type specimens $\frac{1}{4}$ in. diameter and over a $1\frac{1}{2}$ in. gauge length. Pull rods were of molybdenum and testing was in the Baldwin Universal Tensile machine Type PTE-42 with a 5000 lb capacity. Coefficients of linear thermal expansion were determined by dilatometric measurements on rod specimens $\frac{1}{4}$ in. diameter and 2 in. long. The specimens were mounted vertically on an aluminium oxide block in the centre of a Marshall furnace with a sapphire push rod connected to the free end by means of a tantalum cap. Measurements were made under an argon atmosphere. The expansion of the specimens was measured on a Atcotran (linear variable differential transformer) gauge connected to the other end of the sapphire rod (out of the heat zone). Temperature was controlled by means of a Pt–13% Rh/Pt thermocouple.

The hardness of both chloride reduced and intermediate alloy metal was determined by measurements on arc-melted samples using a Brinell standard hardness tester, 500 kg, 10 mm hardened steel ball. The samples were flattened and polished prior to the measurements.

DISCUSSION AND CONCLUSIONS

In general this method of preparing yttrium metal compares very favourably with any described in the literature. On the basis of the bromine insoluble and total rare earth analyses, the metal produced from Reduction (3) was of the order of 99·8 per cent pure. This is the purest yttrium metal yet reported. This is substantiated by its extremely clean microstructure (Fig. 5) as compared to the microstructure of production grade yttrium prepared by the intermediate-alloy process.

Oxygen and nitrogen contamination of yttrium metal produced by this method was approximately the same as that in yttrium from the intermediate-alloy process.

Preparation of yttrium metal by reduction of the chloride with lithium should have commercial application where small quantities of high-grade metal are needed. Preparation in large quantities would require scaled-up studies of both the preparation of anhydrous yttrium chloride and reduction to the metal.

The most difficult portion of this investigation was the area of preparing and evaluating yttrium chloride for reduction. The method employed for the dehydration of yttrium chloride hexahydrate, while usable, is time consuming and expensive from a commercial viewpoint. A study of more efficient methods of obtaining anhydrous yttrium chloride from the oxide is certainly desirable. Casting of "raw" chloride produced in some manageable form is advantageous due to the hygroscopic nature of yttrium chloride, but an evaluation of suitable container materials other than platinum is necessary if large quantities of the fused salt are to be prepared. This evaluation would also be applicable to the elimination of a platinum distillation retort in the purification step. Possible alternative materials may be nickel or nickel-base alloys such as the Inconels or Hastelloys.

Analyses of the raw and distilled yttrium chloride by the methods described in this investigation were experimental to a large degree and point up the necessity for better and more specific analytical methods.

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THE PREPARATION OF STOICHEIOMETRIC FERRITES*

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Abstract—The difficulties encountered in the preparation of pure stoicheiometric ferrites MFe_2O_4 ($M = Mg^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}) are briefly discussed. A new procedure is then described that avoids some of these difficulties. Atomic ratios, Fe/M, very close to the theoretical value of two are obtained by the thermal decomposition of crystallized salts $M_3Fe_6(CH_3CO_2)_{17}O_3OH{\cdot}12C_5H_5N$. The products are ignited in the air at temperatures chosen to yield the correct oxygen content. The products are examined by chemical analysis and the measurement of several physical constants.

THE ferrites include a group of crystalline oxides with the general compositional formula MFe_2O_4. The symbol M can represent magnesium, manganese, iron, cobalt, nickel, copper, zinc and cadmium. The magnetic properties of several of these substances combined with relatively low electrical conductivity compared to the magnetic metals and alloys have created many well-known applications in high-frequency electronic devices. The study of the intrinsic properties of the materials also has led to important new ideas concerning the origin and nature of magnetic phenomena. It seems reasonable that fundamental physical studies should be made on compounds of the highest available purity and homogeneity. A brief review of preparative methods previously used is given below and some of the difficulties encountered in achieving maximum purity and correct stoicheiometry are pointed out. A new procedure is then described in which some of these difficulties are avoided.

PREVIOUS METHODS

In the spinel structure of the ferrites discrete anionic complexes cannot be distinguished; the ferrites MFe_2O_4 are not derived from well-defined water-soluble acids and cannot be crystallized from aqueous solutions.§ The method of preparation usually employed consists simply of preparing an intimate physical mixture of two appropriate oxides and heating this mixture to a temperature sufficiently high to cause the reaction of one solid with the other and the formation of a new phase. If the purity and homogeneity of the product is considered, a number of difficulties arise. Compositions corresponding exactly to the formula MFe_2O_4 are approached with an increasingly refined technique. It is necessary to use the purest, assayed simple oxides, accurately weighed, intimately mixed and reacted without the preferential loss of one reactant or the introduction of non-volatile impurities. Complete homogeneity usually requires that the first product be thoroughly pulverized and ignited a second or third time.

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‡ Lincoln Laboratory, Massachusetts Institute of Technology.
§ Fe_3O_4, $CoFe_2O_4$ and $MnFe_2O_4$ when coprecipitated by alkalis from solutions of soluble salts, although largely hydrous, contain the ions sufficiently ordered to exhibit spontaneous magnetization.

This is particularly true of ferrites prepared from very refractory materials such as MgO.

Several variations of the direct synthesis of ferrites have been devised that make use of substances which yield the component oxides in a very reactive, finely divided condition following thermal decomposition. Summary discussions of ferrite syntheses have been given by ECONOMOS[1], FRESH[2], and WELCH[3].

An interesting synthetic method first described by HILPERT and WILLE[4] appears to have been neglected in recent years. These authors prepared several ferrites by a solid-state, double-decomposition reaction which can be represented by the following equation:

$$M^{2+}Cl_2 + Na_2M_2^{3+}O_4 \xrightarrow{400\text{–}500^\circ C} M^{2+}M_2^{3+}O_4 + 2NaCl$$

This procedure can be used advantageously when the more common methods become difficult as in the preparation of mixed oxides containing FeO or in the preparation of mixed oxides containing very refractory components. We have successfully prepared a very pure $Fe^{2+}Fe_2^{3+}O_4$ ($Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 0{\cdot}3337$) by this procedure and several other mixed oxides including $Fe^{2+}Cr_2^{3+}O_4$, $Fe^{2+}Ti^{4+}O_3$ and $Fe^{2+}Al_2O_4$.

The synthesis of ferrites from mixed oxalates is a very easy one to carry out in the laboratory and in several cases yields homogeneous products in a very short time. It has been demonstrated that ferrous oxalate dihydrate, $FeC_2O_4{\cdot}2H_2O$, can be coprecipitated from boiling solutions of salts with the corresponding oxalates of manganese (II), cobalt (II), nickel (II) or zinc in the form of mixed crystals.[5] The products are finely crystalline, free-flowing powders which are easily handled and contain the iron and other metals mixed on an atomic scale. The mixed oxalates are decomposed to ferrites upon heating in the presence of air; only relatively low temperatures are required except in the case of manganese ferrite. Values for the atomic ratio Fe/M deviating by less than 1 per cent from the theoretical value of two are seldom obtained. This fact is a consequence of small differences in the solubility and the tendency of the oxalates to form supersaturated solutions.

A high ignition temperature is required to produce a single-phase manganese ferrite. At temperatures below approximately 1000°C the material in equilibrium with air is composed of two phases, an Mn_2O_3 phase (c-rare-earth oxide structure) and an α-Fe_2O_3 phase (corundum structure).[6] At higher temperatures (up to ca. 1300°C) a single phase can exist, but it still contains excess oxygen. It is true for all the ferrites, because they contain transition metals which can exist in several oxidation states, that the preparation of a stoicheiometric, single-phase material must take into account phase-composition-temperature-oxygen pressure relationships. PALADINO has determined the phase equilibria for the systems Ni–Fe–O,[7] and Mg–Fe–O[8] in the ferrite region for temperatures 1000 to 1300°C and for oxygen pressures from 10^{-2} to 1 atm. In the preparation of magnetite, $Fe^{2+}Fe_2^{3+}O_4$, which contains a

[1] G. ECONOMOS, *J. Amer. Ceram. Soc.* **38**, 242, 292 (1955).
[2] D. L. FRESH, *Proc. I.R.E.* **44**, 1303 (1956).
[3] A. J. E. WELCH, *Proc. Inst. Elec. Engng.* **104**, Part B, Suppl. No. 5, 138 (1957).
[4] S. HILPERT and A. WILLE, *Z. Phys. Chem.* **18** B, 291 (1932).
[5] D. G. WICKHAM, *M.I.T. Lab. for Insulation Res.* Tech. Report No. 89 (1954).
[6] B. MASON, Dissertation, *Geologiska Föreningens i Stockholm Förhandligar* **65**, 97 (1943).
[7] A. E. PALADINO, *J. Amer. Ceram. Soc.* **42**, 168 (1959).
[8] A. E. PALADINO, Raytheon Mfg. Co., *Research Studies and Investigations of the Solid State Chemistry of Ferrites*, Final Report, Jan. 15, 1958 to Jan. 15, 1959; Signal Corps Contract DA-36-039-sc-74987, DA Project Task No. 0095-ph-58-91.

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single transition metal in two oxidation states, obtaining the correct Fe/M^{2+} ratio and the correct oxygen content can become a single problem. In the preparation described by SMILTENS[9] the oxygen pressure is continuously varied toward lower values as the iron oxide is cooled from high temperature in order to provide the necessary equilibrium conditions. At very high temperatures (>1400°C) in the air the other ferrites MFe_2O_4 are dissociated appreciably with the formation of ferrous iron and elevated oxygen pressures are necessary to maintain stoicheiometry.[5,10–12] The presence of Fe_2O_3 in excess of that represented by MFe_2O_4 enhances the formation of ferrous iron and can produce an increased electrical conductivity.[13] Fine powders, however, which have become dissociated in the air at high temperature are reoxidized if cooled very slowly to lower temperatures.

Success in obtaining the correct Fe/M ratio in most of the procedures mentioned above depends upon beginning with accurately weighed quantities of materials of known composition and bringing about their combination and reaction without disturbing this balance. The procedures described below yield values for the ratio Fe/M very close to 2 : 1 as a natural consequence of the reactions carried out.

EXPERIMENTAL

Preparation of stoicheiometric ferrites

WEINLAND and HOLTMEIER[14] have described the preparation of the double basic acetates $M_4^{2+}Fe_9(CH_3CO_2)_{26}(OH)_9 \cdot 23H_2O$(M = Co, Ni)(I) and $MFe_2(CH_3CO_2)_6(OH)_2 \cdot nH_2O$(M = Mg, Mn, Co, Ni)(II). They have also described the preparation of the compounds $M_3Fe_6(CH_3CO_2)_{17}O_2OH \cdot 12C_5H_5N$(M = Co, Ni)(III) which crystallize upon cooling hot solutions of (I) in pyridine. The latter type compounds we have found to be useful in the synthesis of ferrites. The compounds (III) contain the iron and divalent metal in the ratio of 2 : 1, and can be purified by repeated recrystallization from pyridine. The crystals, in addition to M and iron, contain only organic material which can be decomposed by heating in air. When ignited under the proper conditions, the decomposition product is a ferrite, MFe_2O_4. We have found that the compounds (II) mixed with appropriate quantities of normal acetates, $M(CH_3CO_2)_2$, can be dissolved in pyridine, and from these solutions the compounds (III) will crystallize also: in this case M can be Mg or Mn as well as Co or Ni. The magnesium and manganese compounds were found to give X-ray powder patterns almost identical with that of the cobalt compound and to contain the correct iron to metal ratio. Analogous copper and zinc compounds could not be prepared.

Procedures

1. *Nickel ferrite.* The basic double acetate, $Ni_4Fe_9(CH_3CO_2)_{26}(OH)_9 \cdot 23H_2O$ is prepared according to the method described by WEINLAND and HOLTMEIER[14] from solutions of $Ni(NO_3)_2$ and $Fe(NO_3)_3$ and $Na(CH_3CO_2)_2$. The washed and dried precipitate is dissolved in hot pyridine (see Table 1 for approximate quantities), solution is filtered hot and allowed to cool and to stand for several hours. The yield can be increased by evaporating the solution until crystals begin to form. The large dark-brown crystals of $Ni_3Fe_6(CH_3CO_2)_{17}O_2OH \cdot 12py$ (py = pyridine) which separate on the bottom of the vessel are collected on a suction filter and washed with a few millilitres of cold pyridine. This product is then twice recrystallized from chemically pure pyridine.

The purified pyridinate crystals are crushed and placed in a shallow platinum dish which is carefully heated to drive off the pyridine without permitting a liquid phase to form from which it is possible an iron or nickel-rich phase could segregate. The temperature is then slowly raised to burn off the bulk of remaining organic material. Before the temperature is increased above 200–300°C, the

[9] J. SMILTENS, *J. Chem. Phys.* **20**, 990 (1952).
[10] S. W. KINGSNORTH, Thesis, Univ. of London (1950).
[11] M. W. SHAFER, *I.B.M. J. Res. Dev.* **2**, 193 (1958).
[12] E. W. GORTER, *Proc. I.R.E.* **43**, 1959 (1955).
[13] L. G. VAN UITERT, *J. Chem. Phys.* **23**, 1883 (1955).
[14] R. WEINLAND and H. HOLTMEIER, *Z. Anorg. Chem.* **173**, 49 (1928); GMELIN, *Handbuch der Anorganischen Chemie* (8th Ed.), Eisen, Teil B. System Nummer 59, pp. 1064, 1152, 1157, 1163 (1932).

TABLE 1.—PREPARATION OF THE COMPOUNDS $M_2^{2+}Fe_6(CH_3CO_2)_{17}O_3(OH)\cdot 12C_5H_5N$

Starting materials		Volume of pyridine solvent	No. of recrystallizations	Yield (g)	%
Compound	Quantity (g)				
$MgFe_2(AcO)_8(OH)_2\cdot 10H_2O$ $Mg(AcO)_2\cdot 4H_2O$	69 8·1	500	1	54·1	58
$MnFe_2(AcO)_8(OH)_2\cdot 5H_2O$ $Mn(AcO)_2\cdot 4H_2O$	71 10·5	500	0 1	78 55	70 49
$CoFe_2(AcO)_8(OH)_2\cdot 8H_2O$ $Co(AcO)_2\cdot 4H_2O$	44·7 6·2	500	1	28·5	45
$Co_4Fe_9(AcO)_{26}(OH)_9\cdot 23H_2O$	80	500	2	24	25
$Ni_4Fe_9(AcO)_{26}(OH)_9\cdot 23H_2O$	75	500	2	29	33

material is placed in an agate mortar and carefully pulverized. Again in the platinum dish the powder is heated, finally to 1000°C, always in a liberal supply of air in order to completely oxidize any residual carbonaceous material. The ignition is interrupted a second time to grind the powder in an agate mortar. The ferrite obtained after ignition for 48 hr at 1000°C gives the chemical analyses and properties listed in Table 2.

2. *Cobalt ferrite.* Cobalt ferrite can be prepared in a manner exactly analogous to that for nickel ferrite. It is found that the use of a mixture of the salts, $CoFe_2(CH_3CO_2)_6(OH)_2\cdot 8H_2O$ and $Co(CH_3CO_2)_2\cdot 4H_2O$ (see Table 1) can be used in place of the salt, $Co_4Fe_9(CH_3CO_2)_{26}(OH)_9\cdot 23H_2O$ to prepare the pyridinate. The compounds (II) are prepared with better yields than compounds (I).

3. *Manganese ferrite.* The pyridine solution of manganous acetates appears to be unstable toward oxidation by the air. The preparation is conveniently carried out in the absence of air with the aid of a Sohxlet extraction apparatus. A 1 l., three-necked flask is fitted with the Sohxlet extraction tube and condenser, a gas delivery tube, and a stopper. The extraction-tube has a draw-off tube and a stopcock at the bottom. The acetates are placed in the flask and a slow stream of nitrogen is passed into the flask through the delivery tube and leaves the system through the condenser. When the air has been flushed from the system, hot pyridine is run into the flask to dissolve the acetates and the solution is brought to boiling. The distillate which collects in the extraction tube is drawn off until crystals just begin to form. The nitrogen stream is maintained until the pyridine solution is cool and the crystals of the pyridinate have separated. The recrystallization is carried out in the same manner with this modification: the crystals are placed in a paper thimble held in the extraction tube, so that the solution is filtered before it is siphoned into the flask below. The thimble cannot be used in the first crystallization because the first pyridine solution to form will be sufficiently rich in water to be decomposed by hydrolysis. The final ignition to the ferrite must be carried out at a high temperature and the product quenched through the temperature region where two phases exist (see Table 2) or cooled under an equilibrium oxygen pressure which would have to be continuously varied with decreasing temperature.[1]

4. *Magnesium ferrite.* The compound $Mg_3Fe_6(CH_3CO_2)_{17}O_3\cdot OH$ 12py can be prepared in the manner indicated in Table 1. When ignited it yields a magnesium ferrite.

Chemical and physical measurements

In order to identify the products, each of the ferrites prepared was chemically analysed. The cubic lattice constants were determined with the aid of powder patterns taken with a Philips Norelco diffractometer using Fe-K_α radiation. The magnetization values were determined at 4·2°K in a field of 10,000 oersteds using the vibrating coil magnetometer.[15] The results of these measurements are given in Table 2.

[15] K. DWIGHT, N. MENYUK and D. SMITH, *J. Appl. Phys.* **29**, 491 (1958).

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TABLE 2.—CHEMICAL ANALYSES AND PROPERTIES OF FERRITES PREPARED BY IGNITION OF "PYRIDINATES"

Compound sought	Weight iron (%)		Weight M^{2+} (%)		Mole ratio Fe/M^{2+}	Ignition temp (°C)	Active O eq./mole	Cubic lattice constant a_0(A°)	Saturation magnetic moment* n_B (μ_B/molecule)
	Found	Theory	Found	Theory					
$MgFe_2O_4$	55·69 ± 0·03	55·84	12·41 ± 0·06	12·16	1·954 ± 0·012	1000	0	8·384 ± 0·001	1·37 ± 0·02
$MnFe_2O_4$	48·32 ± 0·02	48·43	23·68 ± 0·03	23·82	2·008 ± 0·005	1300†	0·034	8·512 ± 0·001	4·5 ± 0·1
$CoFe_2O_4$	47·55 ± 0·01	47·60	25·24 ± 0·08	25·12	1·990 ± 0·01	1000	0·004	8·388 ± 0·001	3·57 ± 0·01‡
$NiFe_2O_4$	47·54 ± 0·03	47·65	25·03 ± 0·01	25·05	1·997 ± 0·004	1000	0	8·338 ± 0·001	2·12 ± 0·01

* Measured at 4·2°K in a field of 10,000 oersteds.
† Quenched in nitrogen, contains 0·12 per cent by weight excessive active oxygen.
‡ Cobalt ferrite is not saturated at 10,000 oersteds.

In order to study the electrical conductivity, it was necessary to prepare ceramic specimens. The ferrite powders were pressed into disks approximately $\frac{1}{2}$ in. diameter and $\frac{1}{8}$ in. thick. The magnesium and cobalt ferrite specimens were fired at 1200°C, the nickel ferrite specimens at 1100°C, and all slowly cooled to room temperature. Silver contacts were baked onto the faces of the disks. The disks were placed in an appropriate sample holder and immersed either directly into a constant-temperature, silicone-oil bath or placed in a tube which isolated the sample from the bath. It was discovered that nickel and magnesium ferrites reacted with the oil at temperatures of ca.200°C while cobalt ferrite appeared to be stable. Measurements below room temperature were made by immersing the sample and holder in various freezing mixtures. Direct current resistances as a function of temperature were measured with the aid of a wheatstone bridge above room temperature, with a Kiethly Megohmmeter below room temperature. The results of these measurements are shown graphically in Fig. 1.

RESULTS AND DISCUSSION

The results of the chemical analyses given in Table 2 indicate that the preparative methods described above were reasonably successful for manganese, cobalt and nickel ferrites. The low value for the Fe/Mg ratio (1·954) obtained for magnesium ferrite is believed to be a consequence of the instability of a boiling pyridine solution of magnesium and iron acetates. An attempt to refine the procedure in this respect was abandoned when PALADINO[8] discovered that a composition corresponding to the formula $MgFe_2O_4$ does not appear to be obtainable as a single-phase under ordinary conditions. The composition corresponding to a Fe/Mg ratio equal to 1·95 is single phase and can be written $(MgO)_{0\cdot028}MgFe_2O_4$.

Manganese ferrite contains 0·034 equivalents per mole excess active oxygen when prepared as described above. This corresponds to a formula approximately $MnFe_2O_{4\cdot017}$. A careful X-ray examination failed to reveal the presence of anything but a spinel phase. The correct oxygen content could perhaps be obtained by quenching from a slightly higher temperature.

Chemical analysis of cobalt ferrite also revealed the presence of a small amount of excessive active oxygen, 0·004 equivalent/mole. SMILTENS,[16] and JONKER[17] have shown that a small excess of cobalt in cobalt ferrite will assume a 3+ oxidation state and replace 3+ iron. The formula of the compound listed in Table 2 thus would be $Fe^{3+}[Co^{2+}Co^{3+}_{0\cdot004}Fe^{3+}_{0\cdot996}]O_4$ which gives a ratio Fe/Co equal to 1·988 in agreement with that of $1\cdot990 \pm 0\cdot01$ computed from values obtained by determination of total iron and cobalt.

The lattice constants listed in Table 2 are in very good agreement with the best values given in the literature. Values for $MnFe_2O_4$ reported in the literature have varied widely (8·45–8·55 Å). This is probably caused by differences in composition which depend upon the method of preparation.

The saturation magnetic moments (n_B), with the exception of that for manganese ferrite, are also in good agreement with accepted values. The value of n_B is less sensitive to small departures from stoicheiometry than it is to variations in the thermal history of the sample which influences the distribution of cations between the tetrahedral and octahedral sites of the spinel structure.

The ferrites are semiconductors for which the d.c. resistance can be given by the formula, $\rho = \rho_0 \exp(+q/kT)$ where ρ_0 and q are experimental constants, T is the absolute temperature and ρ is the observed resistance. The value of ρ actually observed for a polycrystalline specimen has limited significance because it depends

[16] J. SMILTENS, *J. Amer. Chem. Soc.* **79**, 4881 (1957).
[17] G. H. JONKER, *J. Phys. Chem. Solids* **9**, 165 (1959).

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greatly upon the physical nature of the specimen, the average grain size, homogeneity, etc. The value of q, which may be obtained from a plot of log ρ vs. $1/T$, is believed to be more characteristic of the material. The graphs of log ρ vs. $1/T$ which were obtained for the ferrites listed in Table 2 are presented in Fig. 1. Manganese ferrite was not

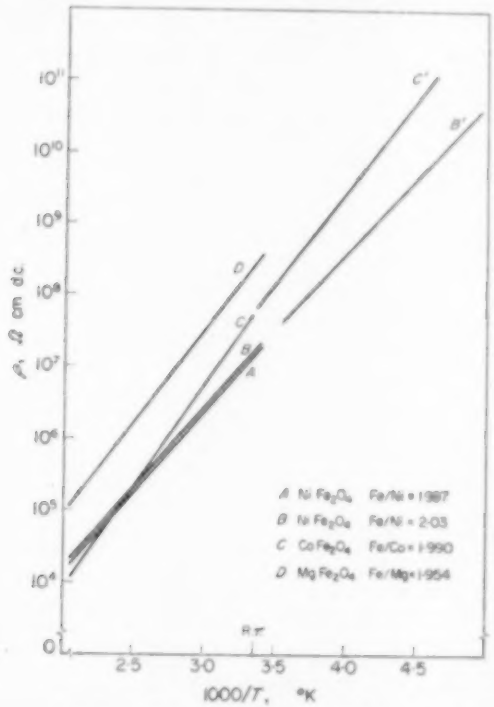

FIG. 1.—Log ρ as a function of $1/T$ for several ferrites.

studied because good ceramic specimens could not be prepared by the method described above for obtaining a nearly correct oxygen stoicheiometry. The values of q given by the high-temperature portions of the curves in Fig. 1 are 0·514 eV, 0·574 eV, 0·454 eV for magnesium ferrite (Fe/Mg = 1·954) cobalt ferrite and nickel ferrite, respectively. The slightly different slopes of the low-temperature portions of the curves is ascribed to experimental error associated with the measurements of resistivities greater than ca. 10^9 Ωcm. These relatively high values for q indicate the absence of any significant amounts of ferrous iron in the products.

JONKER[17] has carried out a very thorough investigation of the semiconducting properties of cobalt ferrite. The value of q which he is able to calculate for the composition $Co^{2+}Co^{3+}_{0.004}Fe^{3+}_{1.996}O_4$ is exactly that which we have observed, 0·57 eV. The Seebeck voltage for a specimen of this same composition is found to be +350 μV/°C again in agreement with the value predicted by JONKER. Physical measurements in this case thus confirm the formula determined by chemical analysis.

It is observed in Fig. 1 that two samples of nickel ferrite with different ratios Fe/Ni, 2·03 and 1·997, give identical values for q. This fact is in accord with the recent phase studies of PALADINO[7] who has found that under equilibrium conditions for oxygen

pressures equal to or greater than 10^{-2} atm it is impossible to prepare single-phase spinels deviating from the stoicheiometric formula $NiFe_2O_4$. The sample with the Fe/Ni ratio equal to 2·03 (prepared from mixed oxalates) should contain a little Fe_2O_3 precipitated between the grains of $NiFe_2O_4$ and offer a slightly higher electrical resistance.[13] The fact that the observed resistance of this material is higher than that of the pure ferrite (Fe/Ni = 1·997) is significant because the density is considerably greater and for this reason should offer a lower resistance (the pure materials exhibited a pronounced reluctance to sinter as pure materials often do).

The matter of trace impurities has not been examined and no spectroscopic analyses have been performed. The "pyridine method", however, would seem to be applicable to the preparation of manganese, cobalt, and nickel ferrites very low in trace impurities, because easily obtainable very pure salts are available as starting materials and the pyridinate precursor of the desired ferrite can be repeatedly recrystallized if necessary.

Acknowledgements—The authors gratefully acknowledge the assistance of R. J. ARNOTT who made crystallographic measurements, N. MENYUK and K. DWIGHT who made the magnetic measurements, and J. B. GOODENOUGH, R. GERMAN, A. WOLD and R. HIGGINS.

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X-RAY STUDY AND ELECTRICAL PROPERTIES OF THE SYSTEM $Ba_xSr_{(1-x)}MoO_3$

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Abstract—The two molybdates (IV) $BaMoO_3$ and $SrMoO_3$ form an unlimited series of solid solutions of the type $Ba_xSr_{(1-x)}MoO_3$. Thermal e.m.f and resistivity measurements on several compounds of this system were performed. The pure compounds $BaMoO_3$ and $SrMoO_3$ were found to have a perovskite structure between room temperature and 1000°C. The cell constants vary linearly with temperature.

EXCEPT for the compounds $Zn_2Mo_3O_8$ and $Mg_2Mo_3O_8$, which MUTHMANN[1] prepared in a somewhat impure form (MCCAROLL *et al.*[2] very recently confirmed these compounds and determined their structure) no molybdates(IV) were reported in the literature, until SCHOLDER and BRIXNER[3] described the preparation of $BaMoO_3$ and $SrMoO_3$ by the hydrogen reduction of their corresponding molybdates(VI). Although these compounds, being of the perovskite type, are structurally identical with their titanium and zirconium analogues, they are quite different in their electrical properties. While the titanates and zirconates are essentially insulators with resistivities in the order of 10^{10} Ω cm the corresponding molybdates are good conductors of electricity, with resistivities in the 10–100 μΩ cm range. Contrary to the titanates and zirconates, the molybdates are deeply coloured. These properties are related to the electronic configuration of the molybdates(IV), which in contrast to the zirconates and titanates, exhibit *d*-electrons in the *N* shell. While there are many semiconducting binary and ternary oxides known, such as NiO, CuO, ZnO, and $GeTiO_3$, with resistivities in the 10^3–10^6 Ω cm range, $BaMoO_3$ and $SrMoO_3$ are metal-like conductors with a positive temperature coefficient of resistivity, much like the tungsten bronzes, although there is no homogeneous range for Sr_xMoO_3 ($x < 1$) as there is for Na_xWO_3.

EXPERIMENTAL

Preparation of reactants

The molybdates(VI), $SrMoO_4$ and $BaMoO_4$ were prepared both by a solid state reaction between MoO_3 (Baker's c.p.) and $SrCO_3$ and $BaCO_3$ (Baker and Adamson's reagent grade) and by precipitation of ammonium molybdate (Mallinckrodt, analytical reagent) with $BaCl_2$ and $SrCl_2$ (Baker and Adamson's reagent grade). Within the analytical errors both preparations were identical. After firing at 1000°C for 2–6 hr, the analysis of these compounds gave 46·55% Ba (calc. 46·20%) and 32·22% Mo (calc. 32·27%) for $BaMoO_4$ and 35·01% Sr (calc. 35·39%) and 38·14% Mo (calc. 38·76%) for $SrMoO_4$. According to SCHOLDER and BRIXNER, $BaMoO_3$ and $SrMoO_3$ were obtained by hydrogen reduction at 980°C and 850°C respectively. The completeness of the reduction was checked by weight loss determinations. The weight loss of the molybdates(VI) upon heating in hydrogen was within a fraction of a percent of the theoretical for conversion to the corresponding

[1] W. MUTHMANN, *Liebigs Ann.* **238**, 136 (1887).
[2] W. H. MCCAROLL, L. KATZ and R. WARD, *J. Amer. Chem. Soc.* **79**, 5410–5414 (1957).
[3] R. SCHOLDER and L. H. BRIXNER, *Z. Naturf.* 10 B, 178 (1955).

molybdate(IV). It was found that even doubling of the reaction time did not result in a reduction beyond the oxidation state(IV), indicating that these compounds are stable with respect to hydrogen under the given conditions.

For the solid solution studies, the compounds were accurately weighed, mixed and ball-milled under argon in a mechanical agate mortar to a particle size of 325 mesh. These mixtures were then pressed at 50–100 tons/in² into bars, ¼ in. square and 2 in. long, and finally sintered under purified argon (Zr/Ti gettered) at 1200–1500° C for 2–4 hr. The specimens obtained in this fashion were used directly for the electrical measurements. Samples for the X-ray studies were cut from the centers of the bars. The densities of the as-pressed bars were approximately 60 per cent of theoretical, which increased to a maximum of 90·8 per cent after vacuum sintering. Some of the data are summarized in Table 1.

TABLE 1.—DENSITY VS. SINTERING TEMPERATURE FOR $SrMoO_3$

Number	Sintering temperature (°C) (Held 2 hr)	Density (g ml^{-1})	% of theoretical
1	As-pressed	3·66	60·0
2	1300	3·93	64·4
3	1450	4·58	75·0
4	1500	5·22	85·6
5	1450 (Vacuum)	5·54	90·8

Sample number 5 was sintered by induction heating *in vacuo*. Arc melting and zone melting were attempted as other means of densification, but in both cases disproportionation occurred, indicating that the compounds do not have a congruent melting point. Despite the fact that vacuum sintering of inductively heated samples produced higher densities, sintering under flowing argon was adopted as a standard preparative technique.

X-ray study

Samples of the composition $Ba_xSr_{(1-x)}MoO_3$ with $x = 1, 0{\cdot}75, 0{\cdot}5, 0{\cdot}25$ and 0 were prepared in the manner described above. X-ray powder diffraction patterns were taken with a Philips 114·6 mm diameter camera at 24·5° C. The samples were sealed in 0·2 mm diameter Lindemann glass capillaries and exposed to the Kα radiation of copper ($\lambda = 1{\cdot}5418$ Å) for between 4 and 6 hr. All readings were taken at constant temperature and corrected for film shrinkage.

TABLE 2.—LATTICE PARAMETERS FOR THE SOLID SOLUTIONS $Ba_xSr_{(1-x)}MoO_3$

x	a_0 (Å)
1·00	4·0404 ± 0·0003
0·75	4·025 0·001
0·50	4·009 0·001
0·25	3·992 0·001
0·00	3·9751 0·0003

Accurate parameters were obtained by extrapolating a_0 vs. $\frac{1}{2}[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$ according to NELSON and RILEY[6]. Table 2 summarizes the lattice parameters; Fig. 1 shows that a Vegard's Law dependence is observed. By an inspection of the nominal values of a_0 plotted against x in Fig. 1, an apparent but slight negative deviation from Vegard's Law is observed. A least-squares treatment of

[6] J. B. NELSON and D. P. RILEY, *Proc. Phys. Soc.* **57**, 160 (1945).

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the data yields the equation, $a_0(x) = (3{\cdot}9756 \pm 0{\cdot}0005) + (0{\cdot}0654 \pm 0{\cdot}0008)x$ (in which the errors are standard deviations), which enables one to state quantitatively that any negative curvature is only apparent and that within the precision of the data Vegard's Law is obeyed. The apparently good Vegard's Law behaviour may be explained by the chemical and steric similarity of the two components.

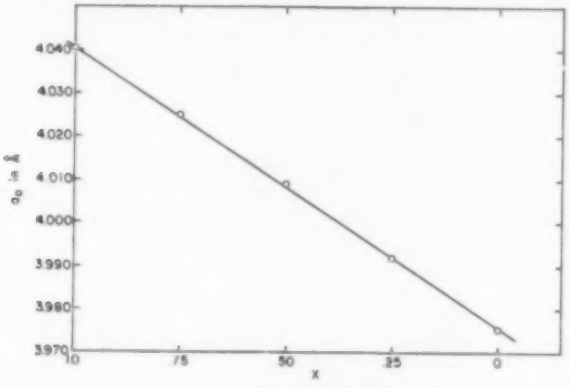

FIG. 1.—Vegard's law dependence for $Ba_xSr_{(1-x)}MoO_3$.

The accuracy of the lattice-constant determinations is limited only by the angular measurements. The reported errors are standard deviations.

The lattice parameters for both $BaMoO_3$ and $SrMoO_3$ were also determined as a function of temperature in a 114·6 mm diameter Chesley high temperature camera. For this purpose the samples were sealed in quartz capillaries, and powder patterns were taken at 200°, 450°, 850° and 1000°C for $SrMoO_3$ and at 150°, 450°, 850° and 1000°C for $BaMoO_3$. The α-1 lines of the split back reflexions

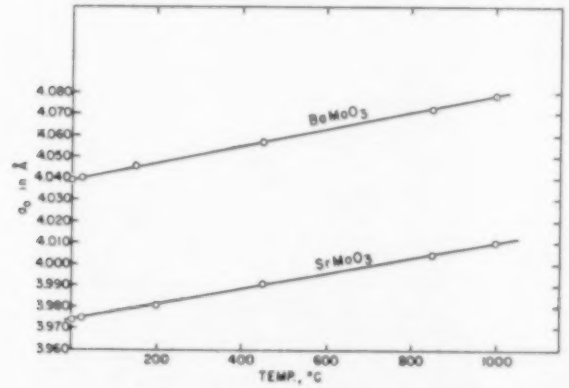

FIG. 2.—Lattice parameters vs. temperature.

were plotted against $\sin^2\theta$ for the parameter determination, which can be expressed as the following function of temperature: for $SrMoO_3$, $a_0 = 3{\cdot}49 \times 10^{-5}T(°C) + 3{\cdot}9746$; for $BaMoO_3$, $a_0 = 3{\cdot}95 \times 10^{-5}T(°C) + 4{\cdot}0395$. Fig. 2 gives a graphical representation of the results.

(All determined parameters were within ±0·001 Å of the calculated values.) It can be inferred from the lack of any new powder lines and also from the lack of a change of intensity ratios that structural changes do not occur. The α-1/α-2 splitting of the lines of the 1000°C pattern was as pronounced and as clear as it was at room temperature, indicating that there was essentially no change in crystallite size. The linear expansion of $SrMoO_3$ is $3{\cdot}62 \times 10^{-5}$ Å/°C; $4{\cdot}00 \times 10^{-5}$ Å/°C for $BaMoO_3$.

Electrical measurements

The d.c. resistivities of the sintered bars of previously described dimensions were measured by the four point method. For the room temperature measurements contacts were made with 32 gauge copper wire imbedded in grooves cut in the sample with a jeweler's saw since soldering onto the ceramic specimen proved very difficult. A 12 V battery was used as power source and the voltage drop was measured with a type K potentiometer. For the high temperature measurements, a Leeds and Northdrop Speedomax six point recorder was used and contacts were made with 0·25 mm platinum wire. A standard resistance in series with the sample served to determine the current. In order to eliminate possible thermal e.m.f's, consecutive readings were recorded every 25 sec at reversed polarity. The samples were heated *in vacuo* (10^{-5} mm Hg) at a uniform heating rate of 1 °C per min.

The estimated accuracy of the data is ±3 per cent; this relatively large uncertainty is due to the errors in measuring both the potential probe spacing and the cross-sectional area of the sample. The reported values are only characteristic of the as-sintered bars, which usually were about 80 per cent of theoretical density. At present on reliable extrapolation to correct for the residual porosity and the pore distribution is available. Table 3 summarizes some typical specific restivity data for bars, sintered at 1200–1500 °C under gettered argon.

TABLE 3.—ROOM TEMPERATURE RESISTIVITIES

Compound	Specific resistivity ($\mu\Omega$ cm)
$SrMoO_3$	78·20
$Sr_{0.75}Ba_{0.25}MoO_3$	73·15
$Sr_{0.50}Ba_{0.50}MoO_3$	50·25
$Sr_{0.25}Ba_{0.75}MoO_3$	80·00
$BaMoO_3$	53·00

Inasmuch as the resistivities depend on the density (as can be seen from Table 4), no reliable relationship between composition and resistivity can be derived, since the densities of the measured bars varied considerably.

TABLE 4.—RESISTIVITY VS. DENSITY FOR $BaMoO_3$

Density	% Theoretical	Specific resistivity ($\mu\Omega$ cm)
5·27	74·4	50·00
5·16	72·7	53·30
4·97	70·2	74·65
4·71	66·6	98·25

An inductively heated, vacuum sintered bar of $SrMoO_3$, with a density of 90·8 per cent showed a resistivity of 24 $\mu\Omega$ cm at room temperature and 2·98 $\mu\Omega$ cm at liquid nitrogen temperature. A typical temperature vs. resistivity curve is represented by Fig. 3. Similar plots for other compositions of the investigated system looked essentially identical. The positive curvature with increasing temperature indicates metallic conduction.

Thermal e.m.f. measurements

In order to check whether the thermoelectric behaviour of these compounds would also be metal-like, the thermal e.m.f. was measured. For this purpose the bars were clamped between two solid

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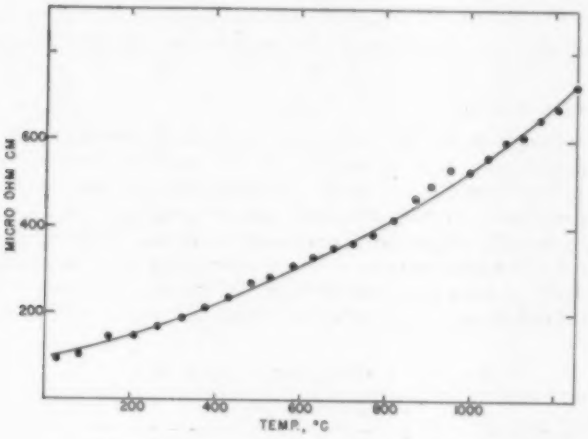

FIG. 3.—Temperature vs. resistivity for $SrMoO_3$.

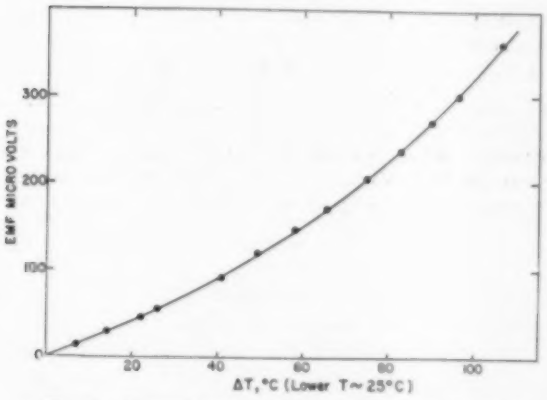

FIG. 4.—Thermoelectric e.m.f. for polycrystalline $SrMoO_3$.

TABLE 5.—SEEBECK COEFFICIENT OF SOME COMPOUNDS OF THE $Ba_xSr_{1-x}MoO_3$ SYSTEM

x	μV/°C (average values)	Conductivity (Ω^{-1} cm^{-1} × 10^{-4}
1	4·00	1·06
0·75	1·52	1·82
0·5	1·40	1·01
0·25	4·48	1·56
0	5·35	1·27

copper blocks, turned from the same piece, one of which was heated by means of a heating tape, the other was water-cooled with a coil soldered on the block. Thermocouples were located in holes drilled to the centre of the bar directly behind the contact face. The voltage was measured with a type K potentiometer. Fig. 4 represents a typical thermal e.m.f. vs. ΔT plot, for $SrMoO_3$. Table 5 summarizes some of the data for the other phases.

Since for most metals $S < 10 \times 10^{-6}$ V/°C and since the thermovoltages observed for the investigated compounds are also in the order of a few microvolts per degree, we again find a metallic behaviour.

Thermal conductivity measurements

The apparatus used for the measurements of the thermal conductivity of the compounds consisted essentially of a vacuum chamber, whose walls acted as a heat sink and to which one end of the bar sample was clamped. To the other end of the sample was soldered an electrical heater whose d.c. input power could be measured. A differential copper–constantan thermocouple was used to measure the temperature drop along the sample under steady state conditions. Both the temperature drop and cross-section and length measurement are subject to 5 per cent error, so that the results taken at room temperature should be accurate to approximately 10 per cent. Measurements were made at room temperature and with liquid nitrogen as a bath. The results are summarized in the following table.

TABLE 6.—THERMAL CONDUCTIVITY DATA

Compound	Thermal conductivity (W/cm°C)	
	25°C	−175°C
$Sr_{0.5}Ba_{0.5}MoO_3$	0·23	0·43
$Sr_{0.75}Ba_{0.25}MoO_3$	0·23	—
$BaMoO_3$	0·24	—

Acknowledgements—The author wishes to thank Dr. F. J. DARNELL for carrying out the thermal conductivity measurements, Dr. R. J. WASILEWSKI for his help in the resistivity measurements, and Messrs. K. R. BABCOCK and A. F. MATERA for their assistance in the X-ray work.

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POTASSIUM TETRA- AND HEXATITANATES*

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(*Received* 15 *October* 1959)

Abstract—Potassium hexatitanate, $K_2Ti_6O_{13}$, m.p. 1370 ± 15°C congruent, is obtained from the K_2O–TiO_2 system in supercritical water or molten KCl in the form of colourless fibrous crystals 0·1–5 μ, averaging about 1 μ, in cross sectional dimensions and up to more than 1 cm in length. Crystals of similar fibrous form obtained from K_2O–TiO_2–KF melt systems in molten KCl appear to be a thermally and hydrolytically unstable potassium oxyfluotetratitanate isostructural with potassium tetratitanate, $K_2Ti_4O_9$. The fibrous potassium oxyfluotetratitanate is converted by water extraction followed by heat treatment to potassium hexatitanate without any change of crystal form. Syntheses, structural characteristics, and physical and chemical properties of new fibrous potassium titanates are described.

POTASSIUM metatitanate K_2TiO_3 and dititanate, $K_2Ti_2O_5$, are well known compounds in the K_2O–TiO_2 system.[1] The loosely bound alkali in these hygroscopic compounds is readily extracted to varying extents by water and acids with some retention of the original crystal form. The resulting products therefore have higher titanate compositions, but it has been questioned[1] whether these compositions represent compounds.

In other reports of higher titanates of potassium, RYAN and KNOFF[2] obtained X-ray diffraction evidence for $K_2Ti_3O_7$ and $K_2Ti_5O_{11}$ in the products of firing TiO_2/K_2CO_3 mixtures in mole ratios of one through six. NEWHAUS *et al.*[3] also observed formation of these same compounds during cooling of $K_2Ti_2O_5$–TiO_2 melts. A hexatitanate composition, in this case of sodium, $Na_2Ti_6O_{13}$, has been mentioned[4] as the product of heating $Na_2Ti_6O_{11}$.

Reported in this paper are

(1) several syntheses of potassium hexatitanate via hydrothermal[3] and simple and flux melt reactions of TiO_2–K_2O and alteration thereto of a potassium oxyfluotetratitanate;[6]
(2) a strikingly fibrous crystal habit of potassium hexatitanate and its dependence upon synthesis conditions; and
(3) some X-ray structural and physical and chemical properties of potassium hexa- and related titanates.

EXPERIMENTAL

Materials

Reactants were analytical reagent grade chemicals from conventional sources. Potassium carbonate and titanium dioxide were dried by heating at 800 C, cooled and stored over phosphorus

* Presented at the 136th meeting of the American Chemical Society, September, 1959.

[1] GMELIN, *Handbuch Anorg. Chemie*, 8 Aufl., Syst. Nr. 41 "Titan" (1951).
[2] L. W. RYAN and J. R. KNOFF, U.S. Pat. 1929521.
[3] A. NEUHAUS, O. SCHMITZ-DUMONT and H. RECKHARD, *Zur Kenntnis der Alkalititanate*, Forschungsberichte des Wirschafts- und Verkehrsministeriums Nordrhein-Westfalen Nr. 190 (1955); O. SCHMITZ-DUMONT and H. RECKHARD, *Monatsh. Chem.* **90**, 134 (1959).
[4] F. VON BICHOWSKY, U.S. Pat. 1731364.
[5] P. L. SALZBERG, T. E. GIER and H. S. YOUNG, U.S. Pat. 2833620.
[6] K. L. BERRY, U.S. Pat. 2841470.

pentoxide in a desiccator. Potassium halides were fused in platinum, cast into a chilled nickel dish, cooled and stored over phosphorus pentoxide or under dry nitrogen.

Apparatus and procedures

Syntheses. Hydrothermal reactions were conducted in collapsible platinum capsules fabricated from 0·25 in. to 1·0 in. diameter platinum tubing having 0·005 in. wall thickness and employing crimped and welded end closures. The capsules were charged with desired proportions of titanium dioxide and of potassium hydroxide in 10 N solution or potassium carbonate and water leaving at least 25 per cent free volume containing air or nitrogen in order to avoid capsule bursting during the heating cycle. The encapsulated reactants were placed in a pressure bomb which was pressured with water to about 1000 atm and then heated. Peak reaction conditions in the range 400–700°C at pressures to 3800 atm were maintained up to about 3 hr followed by slow cooling under pressure to promote crystal growth. The capsules were cut open to obtain the products which were treated with boiling 6 N hydrochloric acid, filtered, washed with water until chloride free and dried in a vacuum oven at about 120°C.

Solid state reactions between ball-milled reactants and melt reactions in bulk and in molten salt solutions and fluxes were conducted in platinum dishes in a muffle furnace or in platinum test tubes supported in mullite tubes in a heavy-duty combustion-tube furnace. Slow cooling for controlling crystal growth was achieved by decreasing the temperatures of the furnaces or, in the latter case, by slowly withdrawing the mullite tube so that the charge was moved through the decreasing temperature gradient in the furnace.

Analyses. For determinations of titanium, samples were chemically dissolved by digesting in hot concentrated sulphuric acid containing ammonium sulphate. The resulting solution was treated with amalgamated zinc in a Jones reductor to reduce titanium to Ti^{3+} which was then titrated with standard (0·1 N) ferric alum solution employing potassium thiocyanate as indicator.[7]

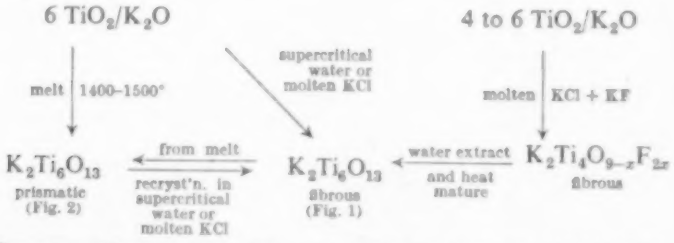
Potassium was determined by flame photometry incorporating an "internal standards" technique[8] as follows. The sample was placed in a platinum vessel and dissolved by digesting with a hot mixture of concentrated hydrofluoric and hydrochloric acids. This solution was divided into six aliquots to five of which potassium chloride was added to give concentrations of 1 through 5 p.p.m. of added potassium. All six solutions were aspirated into a hydrogen–oxygen flame and the emission intensity at 768 mμ determined. From the plot of intensity versus concentration, which is linear, the amount of potassium in the aliquot to which no addition had been made was found by extrapolation.

Differential thermal analyses were conducted employing apparatus similar to that described by Stone.[9] Temperatures to about 1400°C were possible by use of furnace windings, sample holders and thermocouples fabricated from platinum and platinum–rhodium alloys.

X-ray diffraction patterns were obtained with Cu$K\alpha$ radiation. Powder patterns were recorded in a Debye-Scherer powder camera or with a G. E. XRD3 diffractometer. Observations on single crystals were made with a Weissenberg camera and a Buerger precession camera.

RESULTS AND DISCUSSION

The most important syntheses of higher titanates of potassium and interrelationships of compounds and crystal habits to be discussed are diagrammatically illustrated as follows:



[7] W. M. Thornton, *Titanium.* Amer. Chem. Soc. Monograph 33, pp. 145–146 (1927); *A.S.T.M., Triennial Standards* 426 (1930).
[8] T. J. Chow and T. G. Thompson, *Analyt. Chem.* **27**, 18 (1955).
[9] R. R. Stone, *Amer. Ceram. Soc. J.* **35**, 76 (1952).

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As will be evident, potassium hexatitanate has a characteristic structure of relatively high stability but represents here the compositionally stoicheiometric end point which is attainable only under special conditions.

Syntheses of fibrous potassium titanates

Hydrothermal synthesis of potassium hexatitanate. All hydrothermal preparations of potassium titanate yielded products having the fibrous crystal habit (Fig. 1) affording the same characteristic X-ray diffraction pattern regardless of (1) use of potassium hydroxide or carbonate as the alkali source, (2) reactant ratios of TiO_2/K_2O in the range 1/1 to 1/12, and (3) a range of pressure–temperature conditions in the supercritical region. Complete reaction of the titanium dioxide in a given time as detected by microscopic and X-ray examination of the products is favoured by TiO_2/K_2O ratios below $\frac{1}{2}$ and use of the finest particle size ($<1\ \mu$) titanium dioxide. Optimum results were obtained employing reactants ratios of $TiO_2/K_2O = \frac{1}{3}$–$\frac{1}{6}$ at 625°C/3000 atm for 3 hr followed by the slowest practical rate of cooling, at least through the initial range of approximately 200°C.

Potassium dititanate, $K_2Ti_2O_5$, prepared by melting $2TiO_2/K_2CO_3$,[10] is an operable source of both reactants, and is converted in supercritical water to fibrous crystals of potassium hexatitanate and alkali in the aqueous phase.

Analyses for potassium and titanium in the crystals after acid extraction corresponded to the variable composition $K_2O{\cdot}6$–$8TiO_2$ which was also indicated by quantitative materials balances. Such balances were obtained by complete reaction of weighed amounts of titanium dioxide with excess potassium carbonate followed by potentiometric titration of the whole reaction mixture with standard 0·1 N hydrochloric acid to determine excess and extracted alkali and weighing the product to indicate the amount of K_2O combined with the titanium dioxide. Reversible ion exchange properties of the fibrous crystals, described later, indicated the validity of this procedure.

Melt synthesis of potassium hexatitanate. The extracted fibrous potassium hexatitanate from hydrothermal synthesis melted sharply on an electrically heated tungsten ribbon[11] at 1370 ± 15°C and, upon cooling, crystallized to coarse, macroscopic needles of $K_2Ti_6O_{13}$ containing rutile in small amount depending upon the TiO_2/K_2O ratio of the extracted fibres. Potassium hexatitanate in this prismatic habit dissolved to a slight extent in molten potassium chloride and recrystallized therefrom in the original fibrous habit when the crystallization temperature was below approximately 1000°C. Since the equilibrium solubility appears to be less than 1 per cent by weight at temperatures approaching the boiling point of potassium chloride, significant quantities of recrystallized product were prepared in several hours by steady state recrystallization through a temperature gradient in the melt. The prismatic form was maintained in a 1050–1100°C zone in the melt and the fibrous form crystallized continuously in a felted mass from melt zones at 900–1000°C. These fibrous crystals could be scooped intermittently from the melt or recovered from the salt after freezing and dissolving the latter. This temperature gradient recrystallization in molten potassium chloride is also operable on TiO_2/K_2CO_3 products which have been either prereacted in bulk or in the molten potassium chloride. At

[10] A. H. Schulz, Dissertation, Bonn (1947).
[11] W. O. Statton, *J. Chem. Phys.* **19**, 33 (1951).

$TiO_2/K_2CO_3 < 6$ ratios, lower titanates separate from the mother liquor upon freezing. These were separated from the hexatitanate by extraction with molten potassium chloride or acid solutions.

The synthesis of fibrous potassium hexatitanate in molten potassium chloride permitted its isolation without exposure to aqueous extraction and its identification by chemical analysis. Isolation was accomplished by removing fibrous crystals from molten potassium chloride, washing them with fresh portions of the latter followed by expressing and evaporating the considerable imbibed potassium chloride in an air stream at 1200°C. Immediately after disappearance of chloride from the crystals they contained K 13·5, Ti 50·74 per cent; calculated for $K_2Ti_6O_{13}$: K 13·63, Ti 50·10 per cent. As the severity or duration of evaporating conditions was increased beyond the minimum necessary to remove chloride, the composition of the titanate became non-stoicheiometric and alkali appeared in the potassium chloride condensate.

Syntheses of potassium tetratitanates. In an effort to circumvent the low solubility of potassium hexatitanate in molten potassium chloride and the resulting low rate of recrystallization of the prismatic to the fibrous habit, potassium fluoride was added to the potassium chloride melt. Titanate solubility increased progressively with fluoride concentration, and melts of KCl/KF eutectic (55/45 mole per cent respectively) containing up to at least 10 per cent by weight of potassium hexatitanate or equivalent TiO_2/K_2CO_3 were clear and homogeneous at 1000–1100°. Such melts permitted the best control of crystal growth by slow loss of heat from the system at the temperature at which crystals first appeared, usually in the range 980–990°. Although the titanate phases which crystallized from fluoride-containing melts were still fibrous, their X-ray patterns underwent progressive change with increasing fluoride concentration indicating decreasing concentration of hexatitanate having a more poorly ordered structure and development of a new structure at the expense of the hexatitanate. This transition was also promoted by decreasing the TiO_2/K_2O ratio in the melt system from six to four.

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Attempts to isolate this new fibrous phase obtained from fluoride-containing systems for determination of its composition by chemical analysis were unsuccessful because of its thermal and hydrolytic instability. The halides evaporated completely from the crystals during 120 hr in a stream of dry air at 875–950°C but the residue was fibrous hexatitanate according to its X-ray diffraction pattern. Cold water treatment removed the halides completely in 1 hr but the structure was transformed to a new one as indicated by a characteristic, reproducible X-ray diffraction pattern. The structure of the water-extracted crystals was stable at least 72 hr at 600°C, but in 48 hr at 700°C changed to the hexatitanate structure. This change occurred without any energy effect detectable by differential thermal analysis and resulted in formation of rutile byproduct if the non-stoicheiometric composition of the water-extracted fibrous crystals was $TiO_2/K_2O > 6$.

Attempts to synthesize a pure, homogeneous phase structurally identical with the fibres crystallized from K_2O–TiO_2–KCl–KF melts, although not completely conclusive, permit the postulation that they are possibly a potassium oxyfluotetratitanate,* $K_2Ti_4O_{9-x}F_{2x}$. Selected melt reactions in the systems TiO_2–KF, TiO_2–K_2TiF_6

* Schmitz-DuMont and Schulz[13] reported compounds of the type $3\,M_2Ti_2O_5.2MF$ from $M_2Ti_2O_5$–MF systems where M = Rb and Cs. When M = K, however, only a simple eutectic was observed.

[13] O. Schmitz-DuMont and A. H. Schulz, *Monatsh. Chem.* **83**, 638 (1952).

FIG. 1.—Potassium hexatitanate by reacting TiO_2 and KOH in supercritical water.

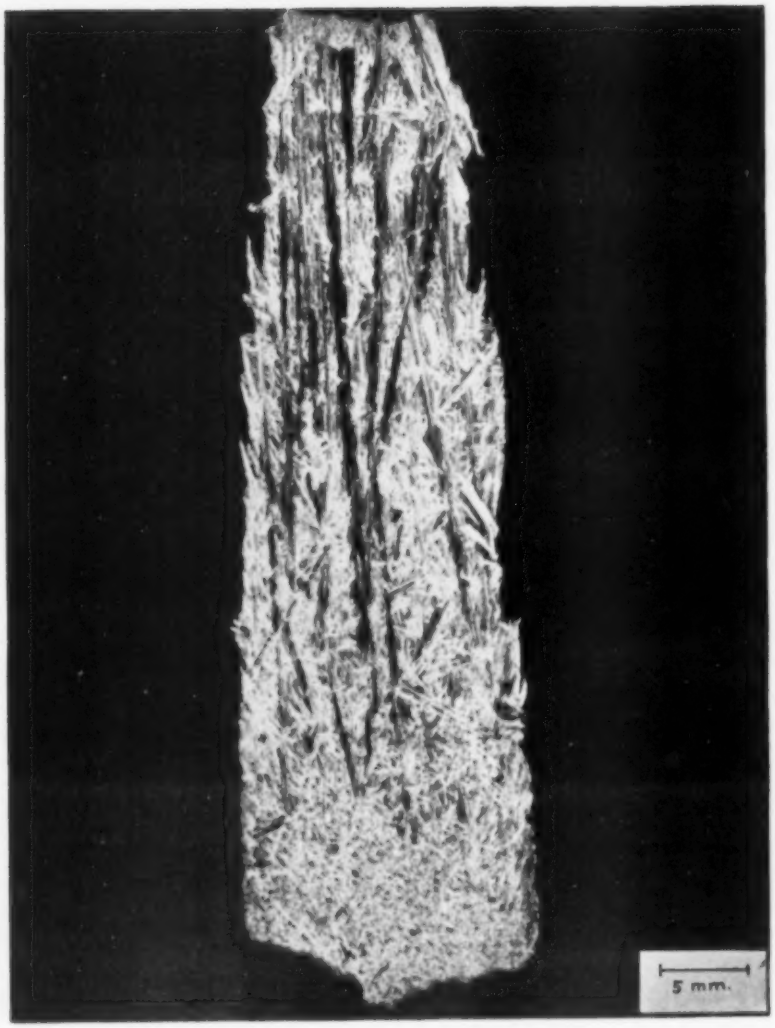

FIG. 2.—Potassium hexatitanate by melt reacting TiO_2 and K_2CO_3.

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and K_2O–TiO_2–KF yielded several new species thought to be oxyfluotitanates but the closest approach to the desired objective from these systems was attained upon crystallizing a melt of $K_2O/6TiO_2/10KF$ which yielded the oxyfluotetratitanate phase and potassium fluoride. At lower potassium fluoride concentrations, its diffraction lines disappeared from the product and the hexatitanate pattern appeared as the pattern of the oxyfluotetratitanate disappeared. There was no X-ray evidence that potassium hexafluotitanate, K_2TiF_6, was a product of potassium fluoride participation in the reaction.

The cleanest pattern identical with that of the fibres crystallized from KCl melts containing appreciable fluoride was encountered upon reacting $4TiO_2/K_2CO_3$ in the solid state[10] at 900°C for 48 hr. This powder product, in contrast to the fibres, retained its structure after 48 hr in boiling water. It is conceivable that one structure might have an oyxgen position plus a vacancy while the second equivalent but less stable structure could contain two fluoride ions in these positions providing the same cell size and charge balance. Hydrolytic instability of the fluoride-containing structure is consistent with that reported[13] for K_2TiOF_4.

X-ray studies

Powder and single crystal diffraction observations of fibrous titanates and associated products were supplemented by similar examinations of a series of TiO_2–K_2O melt products. TiO_2/K_2CO_3 were melt-reacted in integral mole ratios 1 through 7 and the products crystallized from the melts to obtain the best possible crystal size and form. In each case, progress of the reaction was followed by weighings between successive meltings, and proportions of reactants were maintained quantative by potassium carbonate additions when necessary to compensate for loss of alkali by volatilization. Temperatures to achieve melting increased progressively through about 1200–1550°C with reactants ratio and the melts were clear and fluid. Crystallization in every case occurred readily upon cooling, producing lath- and needle-like crystal masses (Fig. 2).

The pattern of the hexatitanate fibre appeared first in ratio 3, increased in intensity through 4 and 5 to a maximum at 6 in which it was the only phase, and occurred with rutile in 7. Concomitant products were potassium dititanate in ratio 3 and potassium tetratitanate, $K_2Ti_4O_9$, identified by solid state synthesis as described previously, in 4 and 5. Ratio 2 product appeared to be the single dititanate phase as reported by SCHMITZ-DUMONT and SCHULZ[12]. As these workers have reported, complete loss of CO_2 from ratio 1 mixtures can not be readily achieved without substantial volatilization of alkali and the product appears to be a mixture of potassium di- and metatitanates resulting, according to NIGGLI[14], from the following equilibrium

$$K_2CO_3 + K_2Ti_2O_5 \rightleftharpoons 2K_2TiO_3 + CO_2.$$

The most characteristic portions of powder patterns of the four observed potassium titanates are listed in Table 1. Data for two preparations of potassium metatitanate are essentially identical but have relatively few features in common with patterns reported earlier by HANNAWALT *et al.*[15] and by SCHMITZ-DUMONT and

[12] H. GINSBERG and G. HOLDER, *Z. Anorg. Chem.* **190**, 407 (1930); **196**, 188 (1931); **201**, 193 (1931).
[14] P. NIGGLI, *Z. Anorg. Chem.* **98**, 241 (1916).
[15] J. D. HANAWALT, H. W. RINN and L. K. FREVEL, *Industr. Engng. Chem.* (*Analyt.*) **10**, 500 (1938).

Schulz[12]. Both of the latter patterns contain lines which might indicate higher titanate components. Except for the longest spacing, our pattern for the dititanate agrees reasonably well with that reported by Schmitz-DuMont and Schulz[12]. The pattern of Barblan[16], obtained from rotation photographs of a single crystal reported to be the dititanate on the basis of reactants ratio, agrees with our potassium hexatitanate pattern rather than that of the dititanate.

Table 1.—X-ray diffraction powder pattern data for potassium titanates

K_2TiO_3				$K_2Ti_2O_5$					
d(Å)	Rel. int.	d(Å)	Rel. int.	d(Å)	Rel. int.	d(Å)	Rel. int.	d(Å)	Rel. int.
7·02	22	1·91	51	6·65	100	2·38	2	1·35	2
5·73	40	1·85	11	4·72	5	2·18	50	1·32	4
3·025	26	1·80	15	3·29	33	1·92	7	1·31	3
2·94	76	1·74	16	3·10	12	1·89	6	1·23	4
2·73	25	1·67	19	3·08	20	1·76	2	1·21	2
2·64	100	1·59	15	2·82	11	1·635	15	1·19	2
2·50	24	1·46	10	2·76	2	1·61	2	1·17	2
2·26	83	1·43	8	2·66	5	1·59	4	1·10	2
2·11	20	1·38	11	2·64	9	1·57	2	1·06	2
2·025	26			2·59	3	1·56	3		
				2·44	3	1·53	7		

$K_2Ti_4O_9$				$K_2Ti_6O_{13}$			
d(Å)	Rel. int.	d(Å)	Rel. int.	d(Å)	Rel. int.	d(Å)	Rel. int.
8·66	100	2·09	32	8·93	10	2·79	23
6·15	43	1·89	28	7·69	100	2·70	28
3·93	11			6·41	69	2·64	7
3·74	13			4·48	8	2·575	23
3·67	9			3·83	4	2·10	32
3·17	45			3·77	4	2·08	32
2·94	51			3·67	18	2·03	3
2·87	43			3·195	7	1·995	4
2·79	9			3·045	47	1·95	3
2·71	23			2·98	60	1·90	26
2·65	38			2·97	66		
2·19	32			2·90	7		

Structure characteristics determined from X-ray data on single crystals are listed in Table 2. Melt products generally furnished the largest and most easily manipulated crystals, but contained troublesome occlusions when selected from polyphase products. Fibrous crystals were clean but presented obvious mounting and alignment difficulties.

Properties of fibrous potassium hexatitanate

Crystal habit. The condition common to the different syntheses of fibrous potassium titanates is the growth of crystals under very high degrees of undercooling.

[16] F. F. Barblan, *Schweiz. Min. u. Petr. Mitt.* **23**, 295 (1943).

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TABLE 2.—STRUCTURE DATA ON VARIOUS POTASSIUM TITANATES FROM X-RAY OBSERVATIONS ON SINGLE CRYSTALS

Compound	Source	Quality	Dimensions*				Density		Symmetry	Space group
			a_0(Å)	b_0(Å)	c_0(Å)	β	Obs.†	Calc. (moles/unit cell)		
K_2TiO_3	TiO_2/K_2CO_3 melt crystallized	Poor because of occusions and instability	6·96	10·0	5·45	—	—	3·06(4)	Ortho-rhombic	
$K_2Ti_2O_5$	$2TiO_2/K_2CO_3$ melt crystallized	Excellent	11·35	3·80	6·63	99·8	2·91	3·00(2)	Mono-clinic	C 2/*m*
$K_2Ti_4O_{9-x}F_{2x}$	$6TiO_2/K_2CO_3$/10KF melt crystallized	Very poor, probably poly-crystalline	12·74	3·80	8·94	104	—	3·27(2)	Mono-clinic	
—	Foregoing, hot-water-extracted	Very poor	12·1	3·80	8·82	99	—	—	Mono-clinic	
$K_2Ti_6O_{13}$	Hydrothermal fibre, and 3/1 and 6/1 TiO_2/K_2CO_3 melt crystallized	Good	15·60	3·80	9·13	99·6	3·58	3·58(2)	Mono-clinic	C 2/*m*

* Film shrinkage errors are assumed to be negligible.
† Densities measured by Archimedes principle employing a hydrocarbon immersant.

Thus, in the case of potassium hexatitanate, the undercooling or differential between growth temperature and melting point was at least about 750° in the hydrothermal synthesis and about 350° during the crystallization from molten potassium chloride. Potassium hexatitanate, therefore, appears to provide a dramatic example of a phenomenon first recognized by Tammann[17], namely, that growth rates of crystallographic directions of some anisotropic crystals are gradually differentiated with increasing degree of undercooling and fibrous forms tend to develop and bear on their ends the faces of greatest crystallization rate.

X-ray diffraction revealed that individual fibres of potassium hexatitanate are single crystals with the *b* axis parallel with the fibre axis. Cross-sectional dimensions of fibres prepared by the various methods described are similar and range 0·1–5 μ with the average about 1 μ. Fibre lengths are markedly dependent upon the control of crystal growth, density of the growth and entanglement of the fibres, and the severity of mechanical treatment to disperse the crystals. Maximum lengths to about 20 mm have been observed in samples appropriately prepared and handled, but ordinarily about 80 per cent of the fibres are less than 2 mm long after complete dispersion by shear in aqueous suspension.

Stability. Of the potassium titanates which have been described, potassium hexatitanate appears to be the most stable. One of the most obvious characteristics of this class of compounds is the loose binding of the alkali, which can be removed by extraction or volatilization. The ease of alkali removal, however, decreases markedly in going from the lower to the higher titanates, and the tendency to maintain structural order upon loss of the alkali increases. Thus, potassium meta- and dititanates are completely decomposed relatively rapidly by water or dilute acids leaving amorphous titania,[14] whereas fibrous hexatitanate, despite relatively high surface/volume ratios, still retained most of its alkali after 18 weeks of continuous extraction by boiling water. After this time, alkali extraction was still detectable, however. The anatase structure of titanium dioxide is the residual phase.

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At temperatures above 1000°C, the vapour pressure of alkali over fibrous potassium hexatitanate becomes detectable. As a result, the material is converted without appreciable change in appearance to rutile. This conversion occurs at very low rates depending upon the rate of removal of the alkali vapour by such conditions as high vacuum and proximity of acidic, alkali scavenging substances.

Direct action of molten boric oxide at 500°C on fibrous potassium hexatitanate extracted 88 per cent of its alkali content in 4 hr, leaving anatase. The hexatitanate fibres are dissolved by hydrofluoric acid solutions, sulphuric acid near its boiling point, fused $NaHSO_4 \cdot H_2O$ and 6 N HCl during several days of boiling.

Tests of the reversibility of cation exchange occurring between short-term extraction of potassium hexatitanate with 6 N HCl at 100°C and potentiometric titration with 0·02 N NaOH showed immediately reversible capacities of only 3–4 meq/100 g in fibrous crystals having a specific surface area of 11 m^2/g, determined by N_2 adsorption in the B.E.T. method. There was a small but steady decrease of reversible cation exchange capacity in successive cycles indicating some attrition of exchange sites. A reversible floc → sol transition occurred upon passing pH 9 during the titration and very dilute suspensions became feebly peptized. Such dispersions

[17] G. Tammann, *Lehrbuch der Metallographie*. Leopold Voss, Leipzig (1914).

were unstable and tended to flocculate during several days with ordering of the fibres into microscopic, yarn-like flocs (Fig. 1).

Thermal. Differential thermal analysis curves for potassium hexatitanate are featureless up to its melting point indicating no phase transformations, abrupt loss of alkali in confined samples, or appreciable hydroxyl groups within its structure. It is probable, however, that hydroxyl groups exist on the surface of acid treated products because samples dried to remove adsorbed water reacted with triphenylchlorosilane yielding hydrophobic fibres. The concentrations of hydroxyl groups was apparently too low to be detected by infra-red spectra. Only characteristic absorption bands at 10·56–10·70 and 13·05–13·22 μ were found.

Suspensions of fibrous potassium hexatitanate in liquid media can be filtered to deposit strong, homogeneous, felted structures. Such forms and their potential utility, particularly as thermal insulation, have been described by GULLEDGE[18].

Titanates of other alkali metals

Other alkali metals have been briefly examined in selected syntheses described for the higher potassium titanates. The behaviour of sodium appeared parallel with that of potassium, and fibrous sodium hexatitanate, made in supercritical water and in molten sodium chloride, is apparently isomorphous with its potassium analogue. The cell dimensions of sodium hexatitanate are $a_0 = 15{\cdot}13$ Å, $b_0 = 3.80$ Å, $c_0 = 9{\cdot}21$ Å and $\beta = 99{\cdot}2°$.

Fibrous rubidium and cesium titanates were obtained in reactions of the carbonates and titanium dioxide in supercritical water.

Acknowledgments—Suggestions of Dr. P. L. SALZBERG and assistance by Dr. T. E. GIER in conducting some hydrothermal reactions are gratefully acknowledged.

[18] H. C. GULLEDGE, Abstracts of Papers presented at the 135th Meeting of the American Chemical Society (1959).

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 240 to 246. Pergamon Press Ltd. Printed in Northern Ireland

CRYSTAL CHEMISTRY OF THE HYDRATES OF SODIUM TRIMETAPHOSPHATE*

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Abstract—Cell dimensions and the method of preparation are reported for $Na_3P_3O_9$, $Na_3P_3O_9.H_2O$, $Na_3P_3O_9.1{\cdot}5H_2O$, $Na_3P_3O_9.3H_2O$ and $Na_3P_3O_9.6H_2O$. The existence of neither $Na_3P_3O_9.0{\cdot}5H_2O$ nor polymorphic forms of $Na_3P_3O_9$ and $Na_3P_3O_9.H_2O$ previously reported by others could be verified.

POLYMORPHIC forms of both anhydrous[1] and monohydrate[2] sodium trimetaphosphate have been reported in the literature. The reports are based almost entirely on unindexed X-ray powder patterns. Without single crystal X-ray data, mixtures of compounds are easily mistaken for pure materials when the powder technique is used. We were interested in the possible existence of stereoisomers[3] of the trimetaphosphate ring and initiated this study to obtain polymorphic crystals which might contain different stereoisomers of the anion. Unfortunately, we were unable to verify the existence of the polymorphic forms.

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MATERIALS AND METHODS

Two sources of sodium trimetaphosphate were used. Dr. E. J. GRIFFITH kindly furnished sodium trimetaphosphate prepared at Monsanto Chemical Company on a pilot-plant scale from commercial insoluble sodium metaphosphate. Recrystallization eliminated small amounts of insoluble metaphosphate. Sodium trimetaphosphate was also prepared by heating sodium dihydrogen orthophosphate[4] for 5 hr at 530°C. The product was purified by salting out solid sodium trimetaphosphate with NaCl from a saturated solution and then by several recrystallizations. The formula weights of the various hydrates and the absence of weak acid impurities were established by an acid-base titration of trimetaphosphoric acid prepared from a weighed sample of the sodium salt by ion exchange with the acid form of Amberlite IR-120(H) resin. Phosphorus[5] analyses confirmed the formula weight.

A powder camera (diameter = 114·59 mm), a Buerger precession camera, and a Weissenberg camera (diameter = 57·30 mm) were used for the X-ray studies. CuK_α radiation (λ = 1·5418 Å) was employed.

The preparation of each of the hydrates studied is given in considerable detail because slight variations in procedure frequently result in mixtures. Other conditions for obtaining the hydrates in reasonable purity will be given in the next section.

* Based on a thesis submitted by Helen M. Ondik in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

‡ Present address, National Bureau of Standards, Washington 25, D.C.

[1] R. W. LIDDELL, *J. Amer. Chem. Soc.* **71**, 207 (1949).
[2] E. THILO and M. WALLIS, *Chem. Ber.* **9**, 1213 (1953).
[3] R. J. GROSS, J. W. GRYDER and G. DONNAY, Abstracts of Papers presented at the 128th Meeting of the American Chemical Society, p. 11R, September (1955).
[4] R. N. BELL, *Inorganic Synthesis* (Edited by L. F. AUDRIETH), Vol. 3, pp. 103–6. McGraw-Hill, New York (1950).
[5] W. F. HILLEBRAND and G. E. F. LUNDELL, *Applied Inorganic Analysis* pp. 546–547. John Wiley, New York (1929).

$Na_3P_3O_9$

Single crystals of the anhydrous material were prepared by heating a pure sodium trimetaphosphate to above the melting point (about 650°C) and then cooling slowly at a rate of 5–10°C an hour. At 550°C the completely solidified sodium trimetaphosphate was removed from the furnace. Cleavage fragments were taken from the matrix for study.

$Na_3P_3O_9.H_2O$

The pure monohydrate was prepared by precipitation from approximately 100 ml of a solution in which the concentration of trimetaphosphate varied from 5 to 25 per cent. An equal volume of ethanol was added at the rate of approximately four drops per second (1 drop = 0·1 ml) with constant stirring at 50–60°C. Large well-formed crystals (0·2 mm across) were grown by evaporating a saturated solution at 60°C. Other hydrates, however, contaminated the product.

$Na_3P_3O_9.1{\cdot}5H_2O$

The pure sesquihydrate can be precipitated from a 10 per cent solution by the extremely slow addition of an equal volume of ethanol at 30°C. The alcohol must be added with constant stirring and slowly enough so that the volume of the solution is doubled in about an hour. Large crystals (0·5 mm across) can be grown by evaporation at 30°C but pure material is not always obtained.

$Na_3P_3O_9.3H_2O$

The trihydrate was made by precipitation from a 5 to 10 per cent solution (ca. 100 ml) at 20°C by the rapid addition of an equal volume of ethanol with vigorous stirring. The product should be filtered immediately after precipitation, since it is not stable in contact with the solution. The compound effloresces readily in air.

$Na_3P_3O_9.6H_2O$

The hexahydrate can be obtained by precipitation with an equal volume of ethanol from an almost saturated solution at 0–20°C. The rate of addition of alcohol does not affect the identity of the product but slow addition will permit the formation of large crystals (0·5 mm).

RESULTS

$Na_3P_3O_9$

The single crystal X-ray study gave the following results. Space group: P2*cn* (*C2v*-9) or P*mcn* (*D2h*-16). Cell dimensions: $a = 7{\cdot}93$ Å, $b = 13{\cdot}14$ Å, $c = 7{\cdot}75$ Å, $V = 808{\cdot}4$ Å^3, all lengths $\pm 0{\cdot}3$ per cent. Density: 2·49 g/cm^3 (observed), 2·52 g/cm^3 (calculated with Z, number of formula units per cell, equal to four).*

The observed powder pattern is in good agreement with that reported by COBRIDGE and TROMANS[6]. All lines below $2\theta = 46°$ are indexed. The maximum deviation between observed and calculated values is 0·2° with an average deviation of 0·08°.

In addition to the procedures given above, the anhydrous material may be prepared by the efflorescence of the hexahydrate or trihydrate under conditions of low humidity. It may also be prepared, usually contaminated with other hydrates, by precipitation from a saturated solution with ethanol or NaCl at room temperature (ca. 25°C). The solid phase in equilibrium with a saturated solution at 60°C is the anhydrous salt, but the monohydrate is formed first.

$Na_3P_3O_9.H_2O$

The crystals of the monohydrate show combinations of two rhombic prisms that simulate a tetragonal bipyramid. Titration data yielded formula weights of 324·2 and

* The calculated powder pattern for this and the other compounds reported is available on request.

323·3 (calc. 323·95). The phosphorus analyses gave 28·83 and 28·71 per cent P (calc. 28·68%).

The single crystal X-ray study gave the following results. Space group: P2*cn* (*C2v*-9) or P*mcn* (*D2h*-16). Cell dimensions: $a = 8{\cdot}53$ Å, $b = 13{\cdot}21$ Å, $c = 7{\cdot}58$ Å, $V = 854{\cdot}3$ Å^3, with all lengths $\pm 0{\cdot}3$ per cent. Density: 2·49 g/cm^3 (observed), 2·52 g/cm^3 (calculated with $Z = 4$).

The observed powder pattern was in good agreement with that reported by COBRIDGE and TROMANS[6] except that the weak lines observed by these workers at

TABLE 1.—POWDER PATTERN OF $Na_3P_3O_9.1{\cdot}5H_2O$

d	Intensity	*d*	Intensity
10·4	*s*	3·16	*m-s*
6·2	*w-m*	3·10	*m-s*
5·53	*vs*	3·02	*m*
5·18	*m*	2·74	*vs*
4·72	*s*	2·68	*w*
4·39	*vw*	2·60	*s*
4·00	*vvw*	2·58	*s*
3·77	*m-s*	2·42	*m*
3·52	*vvw*	2·27	*w*
3·45	*m-s*	2·21	*w*
3·31	*w*	2·15	*w-m*
3·23	*w-m*		

d spacings of 3·21, 2·35 and 2·23 were not present in our photographs and can not be indexed using the cell dimensions reported above. In addition we find a strong line at $d = 3{\cdot}57$ instead of 3·62. The closest calculated spacing is 3·58. All lines in our pattern below $2\theta = 48°$ are indexed, with the experimental values being within 0·2° of the calculated values except for one line which deviates by 0·25°. The average deviation is 0·09°.

In addition to the procedures given above, the monohydrate may be obtained from the efflorescence of the tri- and hexahydrates under conditions of high humidity.

$Na_3P_3O_9.1{\cdot}5H_2O$

The crystals of the sesquihydrate are very thin elongated plates. Titration formula weights were 332·9 and 334·4 (calc. 332·98). The phosphorus content was 27·91 and 27·90% (calc. 27·91%).

The single crystal data yielded the following results. Space group: $A2_122$ (D2-5). Cell dimensions: $a = 11{\cdot}05$ Å, $b = 20{\cdot}70$ Å, $c = 8{\cdot}01$ Å, $V = 1832$ Å^3, all lengths $\pm 0{\cdot}3\%$. Density: 2·40 g/cm^3 (observed), 2·41 g/cm^3 (calculated with $Z = 8$).

The powder pattern is given in Table 1. The lines reported are indexed with a maximum deviation of 0·20 in 2θ and an average deviation of 0·06°. In addition to the lines given in Table 1, a very weak line was observed at $d = 2{\cdot}93$ and a weak line

[6] D. E. C. COBRIDGE and F. R. TROMANS, *Analyt. Chem.* **30**, 1101 (1958).

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at $d = 2{\cdot}34$. The 2·93 line is probably a β-reflexion of the strong 2·60 line. The β-reflexions of the other very strong lines would coincide with other lines and would not be observed. The 2·34 line remains unexplained.

$Na_3P_3O_9.3H_2O$

Single crystal work could not be done on this hydrate for several reasons. Suitable crystals could not be grown because the trihydrate changes to the sesquihydrate or monohydrate when it stands in contact with the mother liquor. The filtered crystals lost water to form the anhydrous or monohydrate compound. The lifetime of the very thin diamond-shaped plates is no more than eight hours.

TABLE 2.—POWDER PATTERN OF $Na_3P_3O_9.3H_2O$

d	Intensity	d	Intensity
12·6	*vs*	2·30	*w*
6·4	*s*	2·84	*w*
5·21	*s*	2·78	*m*
4·48	*vvw*	2·71	*m*
4·21	*m-s*	2·58	*m-s*
3·90	*vvw*	2·52	*vvw*
3·56	*vw*	2·28	*vw*
3·45	*m*	2·25	*vw*
3·40	*w*	2·01	*m*
3·15	*m-s*		

When examined under the polarizing microscope the "platy" crystals seem to be uniaxial with $\omega = 1{\cdot}44$. They appear isotropic when lying flat on the stage; they are birefringent when standing at an angle to the stage. No interference figure could be obtained. Measurements of the angles between the edges bounding the plate do not indicate either the tetragonal or the hexagonal system. The powder pattern, however, is relatively simple and can be indexed by means of the Bunn charts for the tetragonal system. The cell dimensions determined from the Bunn charts are $a = 12{\cdot}86$ Å, $c = 12{\cdot}63$ Å. The powder pattern is given in Table 2.

The average d spacings obtained from eight films are reported. A few very weak lines which appeared on only three or four of the films have not been entered on the table. On all of the films a very very weak line is observed at $d = 5{\cdot}53$ which cannot be properly indexed. This line does correspond to a very strong line in the pattern of the sesquihydrate which is presumably coprecipitated in very small quantity.

The lines reported in the table have a maximum deviation in 2θ of 0·2° and an average deviation of 0·07°. In order to determine the formula of the salt, the precipitation was carefully and quickly performed, the solid was rapidly filtered, washed with alcohol, and air-dried for an hour. Samples were quickly weighed out and at the same time a powder film taken to ascertain the identity of the salt. Analyses were performed on samples from different preparations. The formula weights were found to be 359·0, 360·7, 360·1 as compared with the calculated value of 359·98. Phosphorus

analyses yielded the values 25·72 and 25·61 per cent as compared with the calculated value of 25·82 per cent.

Using the calculated cell volume of 2089 Å^3, a D/Z ratio can be calculated (D = density, Z = number of formula units per cell) which is equal to 0·286. If $Z = 8$ the density is then approximately 2·3, a reasonable value when compared with the densities of the other hydrates.

$Na_3P_3O_9.6H_2O$

The hexahydrate, like the trihydrate, is unstable when exposed to the atmosphere, effloresing to form the monohydrate or anhydrous $Na_3P_3O_9$, depending on humidity conditions. It is stable, however, for months or longer, if stored under a saturated trimetaphosphate solution at temperatures below 30°C. Large triclinic crystals (2 mm across) can be grown easily. Single crystal work was difficult because of the instability of the compound. Axial ratios and interaxial angles derived from goniometry (by J. D. H. DONNAY, unpublished) combined with one length obtained from precession films (taken by G. DONNAY) yielded the dimensions of a primitive cell, which gave the following DELAUNAY[7] reduced cell:

$a = 9{\cdot}50$ Å, $b = 11{\cdot}03$ Å, $c = 7{\cdot}98$ Å, $V = 704{\cdot}59$ Å^3,
$\alpha = 104°50'$, $\beta = 90°57'$, $\gamma = 117°59'$

The observed density was 1·93 g/cm^3 and the calculated density is 1·95 with $Z = 2$.

Titrations carried out on samples which were quickly filtered and dried yielded formula weights of 415·8 and 414·7 compared with a calculated value of 414·03. The high values probably result from insufficient drying time. The powder pattern is reported in Table 3. The maximum deviation between observed and calculated 2θ values is 0·21°. The average deviation is 0·08°. The powder pattern reported by COBRIDGE and TROMANS[6] is in reasonable agreement with our results. Their observed lines at $d = 7{\cdot}2$ and 6·6 cannot be indexed. CAGLIOTI *et al.*[8] worked on the structure of the hexahydrate and reported cell dimensions obtained from Weissenberg photographs. Their values do not permit indexing of the observed powder pattern. Their cell dimensions, after a Delaunay reduction, are $a = 9{\cdot}88$ Å, $b = 11{\cdot}65$ Å, $c = 8{\cdot}43$ Å, $\alpha = 103°19'$, $\beta = 92°6'$, $\gamma = 119°35'$. The density they report, 1·786, is much lower than our value which agrees with the density of 1·928 reported by Thilo.

DISCUSSION

Professor E. THILO kindly furnished us with a portion of Dr. M. WALLIS' thesis which allowed us to compare our results with his. In the published paper[2] of THILO and WALLIS 2θ values are reported graphically. Table 4 lists d spacings along with the values reported[9] by THILO and HAUSCHILD. It should be noted that the camera used by Thilo has a diameter one-half that of the powder camera used in this laboratory. His error may therefore be estimated as $\pm 0{\cdot}4°2\theta$.

Comparison of the data reported in Table 4 with those for the monohydrate and sesquihydrate reported here indicate that THILO's monohydrate II and sesquihydrate

[7] J. D. H. DONNAY and W. NOWACKI, *Crystal Data* pp. 137–140. Geological Society of America, New York (1954).
[8] V. CAGLIOTI, G. GIACOMELLO and E. BIANCHI, *Atti. Accad. Ital. Rend.* (7), **3**, 761 (1942).
[9] E. THILO and U. HAUSCHILD, *Z. Anorg. Chem.* **261**, 324 (1950).

TABLE 3.—POWDER PATTERN OF $Na_3P_3O_9.6H_2O$

d	Intensity	*d*	Intensity
9·4	*w-m*	3·28	*w*
8·8	*vs* (broad)	3·21	*m*
8·3	*vvw*	3·03	*w*
7·5	*vvw*	2·99	*w-m*
7·0	*vw*	2·91	*w*
6·0	*m*	2·86	*m*
5·43	*w*	2·81	*vw*
5·15	*m* (broad)	2·76	*w*
5·00	*w-m*	2·73	*w*
4·74	*w-m*	2·66	*m*
4·27	*w*	2·60	*w*
4·11	*w-m*	2·52	*vvw*
3·93	*w-m*	2·49	*w*
3·75	*w-m*	2·41	*w*
3·64	*vw*	2·67	*w*
3·56	*w-m*	2·31	*w*
3·48	*w-m*	2·29	*w*
3·40	*vvw*	2·24	*w*
3·35	*w*		

TABLE 4.—COMPARISON OF *d* VALUES FOR POWDER PATTERNS OF THILO'S HYDRATES

1950			1953	
$Na_3P_3O_9.H_2O$	$Na_3P_3O_9.H_2O$ I	$Na_3P_3O_9.H_2O$ II	$Na_3P_3O_9.1{\cdot}5H_2O$	$Na_3P_3O_9.0{\cdot}5H_2O$
5·5 *s*			5·5 *vs*	5·3 *vvs*
5·0 *w*		5·0 *vs*	5·0 *vw*	
4·5 *vs*	4·5 *vs*		4·5 *s*	4·6 *s*
		4·3 *s*		
3·97 *w*	3·97 *w*	3·90 *s*		
			3·70 *vw*	
3·52 *vs*	3·52 *s*	3·52 *vs*		
			3·35 *s*	3·32 *s*
3·25 *vvs*	3·28 *vvs*	3·26 *s*		
3·06 *vvw*	3·06 *vw*		3·08 *vs*	3·06 *vs*
2·86 *vvs*		3·00 *vs*		2·86 *w*
	2·80 *vs*	2·78 *vvs*		
			2·71 *vs*	
2·62 *w*	2·62 *w*			
			2·58 *vs*	2·59 *s*
		2·55 *vvs*		
2·51 *s*	2·50 *s*			
		2·47 *w*		
2·40 *vvw*?	2·40 *vw*		2·40 *w*	2·39 *vw*
		2·35 *s*		
2·31 *s*	2·27 *s*	2·27 *vw*	2·28 *w*	2·26 *w*
2·16 *w*	2·16 *w*	2·13 *s*	2·16 *vw*	2·15 *w*

were impure materials. Many of the lines reported by THILO are actually doublets. We were unable to obtain a salt corresponding to his monohydrate I. His description of the crystals, the method of preparation by precipitating from dilute solution, and the fact that he calls the crystals metastable suggest that he may have obtained the trihydrate. THILO's evaporative procedure for obtaining his "monohydrate I" gave us mixtures of known hydrates. On some patterns of these mixtures lines appeared which do not correspond to those of known salts, suggesting the existence of other hydrates. This possibility should be investigated further.

The cell dimensions reported by THILO for his monohydrate II, corresponding to the monohydrate reported in this work, were obtained from rotation photographs of single crystals. These dimensions agree fairly well with those obtained from precession photographs in this laboratory. The *a* and *c* lengths are so nearly equal that on poorly adjusted rotation films the crystals could well appear to be tetragonal, as he reported, instead of orthorhombic as we found them to be. Indeed the photostatic copies of the films he so generously supplied indicate that the crystals were slightly misaligned.

It is interesting to note the similarity between the powder patterns of the anhydrous $Na_3P_3O_9$ and the monohydrate (Fig. 1). The same lines appear, in the same order, in both patterns. The slightly larger cell dimensions of the monohydrate account for the greater splitting of the 110, 011, and 020 lines and of the 111 and 021 lines in its pattern. These same lines are so close in the anhydrous pattern that on most of the films they appear as single broad lines. Films of mixtures of the two salts show very broad diffuse lines. These results emphasize the extreme care that is necessary in employing X-ray powder patterns as proof of new compounds. Only when single crystal data have been used to index the powder film can one be certain of the conclusions.

The results of this work were used to add support to the identification of the product obtained by GRIFFITH[10] from the neutralization of $Na_2HP_3O_9$ by NaOH. We found that the product was $Na_3P_3O_9.H_2O$.

Acknowledgements—We are indebted to Professor J. D. H. DONNAY and Dr. GABRIELLE DONNAY for their interest and assistance in this study. Professor E. THILO kindly furnished a photostatic copy of a portion of Dr. M. WALLIS' thesis.

The work was supported in part by grant G-2745 from the National Science Foundation. One of us (H. M. O.) was the recipient of a grant-in-aid from the Hynson, Westcott and Dunning Fund for the academic year 1954–1955.

[10] E. J. GRIFFITH, *J. Amer. Chem. Soc.* **78**, 3867 (1956).

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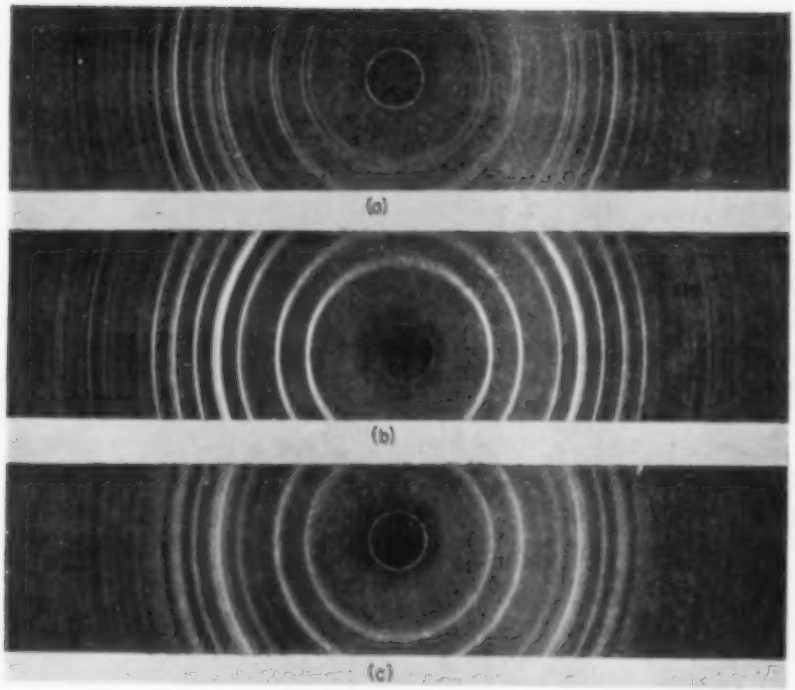

FIG. 1.—Powder patterns for (a) $Na_2P_2O_6.H_2O$, (b) $Na_2P_2O_6$, (c) mixture.

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IONENAUSTAUSCH IN LÖSUNGSMITTELGEMISCHEN—I

ÜBER DIE VERTEILUNG VON URAN ZWISCHEN MINERALSAUREN ALKOHOLISCHEN LÖSUNGEN UND DEM STARK BASISCHEN ANIONENAUSTAUSCHER DOWEX-1

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(*Received* 28 *September* 1959)

Abstract—The present work was designed to furnish data about the anionic behaviour of uranyl ions in mixed solvents. The distribution coefficients for uranium on the strongly basic anion exchanger Dowex 1 have been determined in hydrochloric-, nitric- and sulphuric-acid solutions containing varying amounts of ethyl alcohol.

VON KRAUS und NELSON[1] durchgeführte Untersuchungen über die Adsorption von Uran an stark basischen Anionenaustauschern aus salz-, salpeter- und schwefelsauren Lösungen lieferten den eindeutigen Beweis dafür, dass sechswertiges Uran je nach Art und Konzentration der angewendeten Säure mehr oder weniger stark in Form eines anionischen Komplexes vorliegt, der von stark basischen Anionenaustauschern wie z.B. Amberlite IRA-400, Dowex-1 und -2 festgehalten wird.

Die vorliegende Arbeit wurde durchgeführt, um das Verhalten des Urans in mineralsauren, alkoholhaltigen Lösungen zu untersuchen, und zwar zwecks Feststellung, ob es in derartigen Lösungen ebenfalls negativ geladene Komplexe liefert. Zu diesem Zwecke wurden die Verteilungskoeffizienten des Urans zwischen diesen Lösungen und Dowex-1 bestimmt. Die in der Regel höheren Koeffizienten in alkoholischen Lösungen sind auf den dehydratisierenden Effekt des Alkohols zurückzuführen, wodurch die Stabilität der Uranylkomplexe erhöht, das Gleichgewicht zugunsten des Komplexes verschoben und dementsprechend seine Adsorption am Harz begünstigt wird.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien. Zur Bestimmung der Verteilungskoeffizienten in salzsauren Lösungen wurde der lufttrockene, stark basische Anionenaustauscher Dowex-1 (50 bis 100 mesh; Cl^--Form) verwendet. Für die Versuche in salpeter- bzw. schwefelsauren Lösungen wurde das Harz durch Behandlung mit 2-*n* Salpeter- bzw. 6-*n* Schwefelsäure in die Nitrat- beziehungsweise Sulfatform übergeführt und nach deren Trocknung an der Luft verwendet.

Es wurden salz-, salpeter- bzw. schwefelsaure Uranyl- chlorid-, -nitrat- und -sulfatlösungen genau bekannter Urangehalte und Normalitäten der dem Anion entsprechenden Säuren angewendet.

Der Urangehalt der Lösungen wurde auf polarographischem Wege unter Anwedung der katalytischen Nitratwelle[2] bestimmt. Der verwendete Alkohol war mit Benzin denaturiertes 95%iges Äthanol (wurde als "100 %ig" angesehen). Wie eine Reihe von Kontrollversuchen ergab, störte

[1] K. A. KRAUS und F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Genera*, 1955, Vol 7, p. 113. United Nations (1956).
[2] F. HECHT, J. KORKISCH, R. PATZAK und A. THIARD, *Mikrochim. Acta (Wien)* 1283 (1956).

das bei den Versuchen fast quantitativ am Austauscher adsorbierte Benzin die Uranadsorption nicht.

Verteilungskoeffizienten. Die Werte für die Verteilungskoeffizienten K (Uranmenge/g Harz dividiert durch die Uranmenge/ml der Lösung) wurden unter Anwendung der Gleichgewichtsmethode ermittelt. Gemessene Mengen des lufttrockenen Harzes (Cl^--, NO_3^-- oder SO_4^--Form) und der uranhaltigen Lösungen bestimmter Säurenormalität und Alkoholkonzentration wurden vermischt und 24 Stunden lang unter häufigem Durchschütteln stehengelassen. [Beispiel: 1 g Dowex-1 (Cl^--Form) + 1 ml 4-*n* Salzsäure + 1 ml 4-*n* salzsaurer Uranylchloridlösung (100 μg Uran/ml) + 8 ml Äthanol. Dadurch entsteht eine Lösung, die 0·8-*n* an Salzsäure und 80%ig an Alkohol ist.] Anschliessend wurde jeder Lösung ein aliquoter Teil entnommen, nach dessen Eindampfen das Uran quantitativ bestimmt und daraus der Verteilungskoeffizient berechnet.

Bei allen diesen Berechnungen wurde der Alkohol als ein nicht indifferentes Lösungsmittel angesehen, d.h. die in den Abb. 1, 2 und 3 angegebenen Säurenormalitäten wurden auf die Gesamtlösung (wässrige Säurelösung und Alkohol) bezogen.

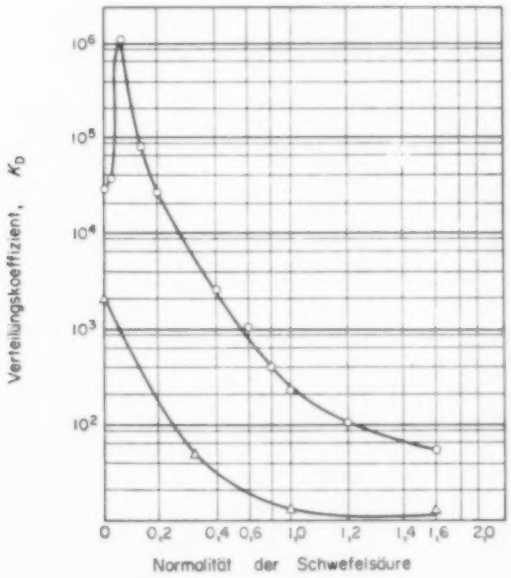

ABB. 1.—○ Uran in "80 %igem" Äthanol.
△ Uran (KRAUS und NELSON).

ERGEBNISSE

In Abb. 1 sind die Ergebnisse unserer in schwefelsaurer alkoholischer Lösung ("80%" Äthanol) durchgeführten Bestimmungen der Verteilungskoeffizienten wiedergegeben. Zum Vergleich wurden die von KRAUS und NELSON[1] in wässrigen Schwefelsäurelösungen gefundenen Verteilungskoeffizienten in die Abb. mit aufgenommen.

Aus dieser Abb. geht deutlich hervor, dass die Adsorption des Urans aus "80 %igem" Alkohol um mehr als 1 Zehnerpotenz grösser ist als in wässeriger Lösung gleicher Acidität. Das in der Kurve auftretende Maximum bei einer Acidität von 0·05-*n* Schwefelsäure konnte bei Abwesenheit von Alkohol nicht festgestellt werden.

In den Abb. 2 und 3 sind die Ergebnisse der in salz- und salpetersauren, alkoholischen Lösungen durchgeführten Bestimmungen der Verteilungskoeffizienten aufgezeigt.

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DISKUSSION

Die in den Abbildungen 1, 2 und 3 gezeigten Versuchsergebnisse zeigen, dass die in schwefelsauren, alkoholischen Lösungen ermittelten Verteilungskoeffizienten (im Vergleich zu den in salz- bzw. salpetersauren, alkoholischen Lösungen gefundenen Werten) am meisten von den in den rein wässerigen Säuren ermittelten Werten,

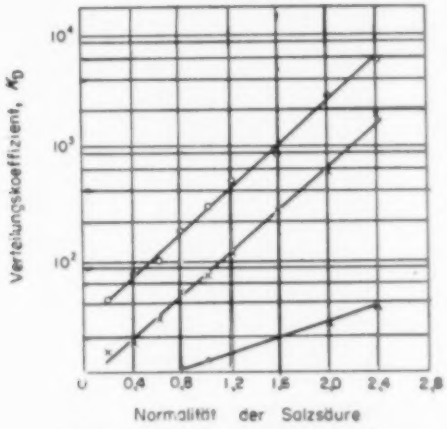

ABB. 2.—○ Uran in "80 %igem" Äthanol.
× Uran in "60 %igem Äthanol".
△ Uran (KRAUS und NELSON).

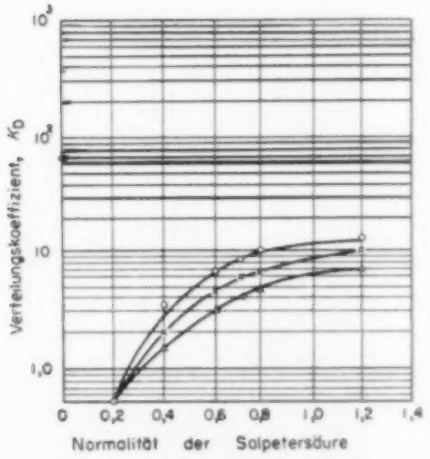

ABB. 3.—○ Uran in "80 %igem" Äthanol.
× Uran in "60 %igem" Äthanol.
△ Uran in "40 %igem" Äthanol.

und zwar im positivem Sinne, abweichen. Die in Abb. 2 gezeigten Resultate sind analytisch von Wichtigkeit, da eine quantitative Uranadsorption schon in 0·6 bzw. 0,8-*n* salzsaurer Lösung ("80%ig" an Alkohol) erfolgt, wenn das Uran auf einer Säule angereichert wird. Ebenso ist infolge der sehr geringen Verteilungskoeffizienten des Urans in salpetersaurer, alkoholischer Lösung eine Trennung von Thorium, das

unter denselben Versuchsbedingungen eine wesentlich grössere Adsorption zeigt, möglich.

Über die Anwendung der aus den vorliegenden Untersuchungen erhaltenen Ergebnisse wird an anderer Stelle berichtet werden.

Abschliessend kann gesagt werden, dass die Uranylionen auch in alkoholhaltigen, mineralsauren Lösungen anionische Komplexe bilden, und zwar gegenüber mineralsauren wässerigen Lösungen in gesteigertem Masse.

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IONENAUSTAUSCH IN LÖSUNGSMITTELGEMISCHEN—II

ÜBER DIE VERTEILUNG VON THORIUM, ZIRKONIUM UND TITAN ZWISCHEN MINERALSAUREN ALKOHOLISCHEN LÖSUNGEN UND DEM STARK BASISCHEN ANIONENAUSTAUSCHER DOWEX-1

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(*Received* 28 *September* 1959)

Abstract—The present work was designed to furnish data about the anionic behaviour of the tetravalent transition elements thorium, zirconium and titanium in mixed solvents. The distribution coefficients for these elements on the strongly basic anion exchanger Dowex-1 have been determined in hydrochloric-, nitric- and sulphuric-acid solutions containing varying amounts of ethyl alcohol.

ÜBER die Adsorbierbarkeit von Thorium aus salzsauren Lösungen an stark basischen Anionenaustauschern berichteten bereits KRAUS *et al.*[1] sowie HYDE[2] und stellten fest, dass praktisch keine Adsorption eintritt. Ähnliche, von CARSWELL[3], DANON[4] sowie YING-MAO CHEN *et al.*[5] in salpetersauren Lösungen durchgeführte Untersuchungen ergaben, dass das Thorium anionische Komplexe liefert und demzufolge eine Adsorption an Anionenaustauschern eintritt, die zur Trennung des Thoriums von anderen Elementen wie z.B. vom Uran[3] oder den seltenen Erden[4] benützt wurde.

Obgleich die Adsorption des Thoriums erst bei relativ hohen Salpetersäurekonzentrationen möglich ist, konnten JENKINS und RICHARDSON[6] sowie SAITO und SEKINE[7] auch den anionischen Charakter des Thoriums in Nitratlösungen und auch Sulfatlösungen beweisen.

Ähnliche Verhältnisse wie beim Thorium findet man auch beim Zirkonium und Titan, nur dass hier die Tendenz zur Ausbildung negativ geladener Chloridkomplexe[8,9,10] bedeutend grösser ist als beim Thorium. Von KORKISCH und FARAG[11] konnte festgestellt werden, dass das Zirkonium aus schwach schwefelsauren Lösungen sehr stark von Amberlite IRA-400 festgehalten wird, wogegen Titan und Thorium keine nennenswerte Adsorption aufweisen.

[1] K. A. KRAUS, G. E. MOORE und F. NELSON, *J. Amer. Chem. Soc.* **78**, 2692 (1956).
[2] E. K. HYDE, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1956, Vol. 7, p. 281. United Nations (1956).
[3] D. J. CARSWELL, *J. Inorg. Nucl. Chem.* **3**, 384 (1957).
[4] J. DANON, *J. Inorg. Nucl. Chem.* **5**, 237 (1958).
[5] YING-MAO CHEN, CHIA-TSUNG LIN und TUNG-HO CHEN, *J. Chinese Chem. Soc.* (*Taiwan*) *Ser.* **11**, 2, 111 (1955); *Chem. Abstr.* **49**, 15619g (1956).
[6] I. L. JENKINS und R. J. RICHARDSON, AERE C/R 1217 (1953).
[7] NOBUFUSA SAITO und TATSUYA SEKINE, *Bull. Chem. Soc. Japan* **30** (5), 561 (1957).
[8] E. H. HUFFMAN und R. L. OSWALT, *J. Amer. Chem. Soc.* **71**, 4147 (1949).
[9] E. H. HUFFMAN, R. C. LILLY und G. M. IDDINGS, *J. Amer. Chem. Soc.* **73**, 4474 (1951).
[10] K. A. KRAUS, F. NELSON und G. W. SMITH, *J. Phys. Chem.* **58**, 11 (1954).
[11] J. KORKISCH und A. FARAG, *Z. Anal. Chem.* **166**, 81 (1959).

Berichte über die Existenz anionischer Titan- oder Zirkoniumnitratkomplexe konnten wir in der entsprechenden Literatur nicht auffinden.

Die vorliegende Arbeit wurde unternommen, um das Verhalten der Elemente Thorium, Zirkonium und Titan in mineralsauren, alkoholhaltigen Lösungen zu untersuchen und festzustellen, ob sich in derartigen Lösungen negativ geladene Komplexe dieser Elemente bilden.

Zu diesem Zwecke wurden die Verteilungskoeffizienten dieser Elemente zwischen solchen Lösungen und Dowex 1 bestimmt.

Über die Verteilung von Uran zwischen mineralsauren alkoholischen Lösungen und Dowex 1 wurde in der I.Mitteilung berichtet;[12] demzufolge gilt auch hier das dort über die Komplexbildung in alkoholischen Medien Gesagte.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien. Zur Bestimmung der Verteilungskoeffizienten in salzsauren Lösungen wurde der lufttrockene, stark basische Anionenaustauscher Dowex-1 (50 bis 100 mesh; Cl^--Form) verwendet. Für die Versuche in salpeter- bzw. schwefelsauren Lösungen wurde das Harz durch Behandlung mit 2-*n* Salpeter-bzw. 6-*n* Schwefelsäure in die Nitrat- bzw. Sulfatform übergeführt und nach deren Trocknung an der Luft verwendet.

Es wurden salz-, salpeter-, bzw. schwefelsaure Lösungen von Thorium, Zirkonium and Titan (Chlorid, Nitrat bzw. Sulfat) von genau bekanntem Gehalt und Normalität der dem Anion entsprechenden Säuren angewendet.

Der Thoriumgehalt der Lösungen wurde auf spektrophotometrischem Wege mit Thoronol[13] bestimmt, der Gehalt der Zirkoniumlösungen durch Titration mit ÄDTA unter Anwendung des Azofarbstoffes Solochrome Violet R.[14]

Die Bestimmung von Titan erfolgte mit der bekannten H_2O_2-Methode.

Der verwendete Alkohol stellte mit Benzin denaturiertes 95%iges Äthanol (wurde als "100 %ig" angesehen) dar. Wie eine Reihe von Kontrollversuchen ergab, störte das bei den Versuchen fast quantitativ am Austauscher adsorbierte Benzin die Adsorption dieser Elemente am Harz nicht.

Verteilungskoeffizienten. Die Werte für die Verteilungskoeffizienten *K* (Menge des betreffenden Elements/g Harz dividiert durch die Elementmenge/ml der Lösung) wurden unter Anwendung der Gleichgewichtsmethode ermittelt. Gemessene Mengen des lufttrockenen Harzes (Cl^--, NO_3^-- oder SO_4^{2-}-Form) und der thorium-, zirkonium-oder titanhaltigen Lösung (salz-, salpeter-oder schwefelsaure alkoholische Lösungen bestimmter Säurenormalität und Alkoholkonzentration)* wurden vermischt und 24 Stunden lang unter häufigem Durchschütteln stehengelassen. Anschliessend wurde jeder Lösung ein aliquoter Teil entnommen und nach dessen Eindampfen das betreffende Element quantitativ bestimmt und daraus der Verteilungskoeffizient berechnet.

Bei allen diesen Berechnungen wurde der Alkohol als ein nicht indifferentes Lösungsmittel angesehen, d.h. die in den Abb. 1, 2 und 3 angegebenen Säurenormalitäten wurden auf die Gesamtlösung (wässrige Säurelösung und Alkohol) bezogen.

ERGEBNISSE

In Abb. 1 sind die Ergebnisse unserer in salpetersauren alkoholischen Lösungen ("80, 60 und 40%" Alkohol) mit Thorium und Zirkonium durchgeführten Bestimmungen der Verteilungskoeffizienten wiedergegeben. Zum Vergleich wurden die von CARSWELL[3] und DANON[4] in wässerigen Salpetersäurelösungen gefundenen Verteilungskoeffizienten für Thorium in die Abbildung mit aufgenommen. Eine

* (Beispiel: 1 g Dowex-1 (NO_3^--Form) + 1 ml 6-*n* Saltpetersäure + 1 ml 6-*n* salpetersaure Thoriumnitratlösung (100 μg Thorium/ml + 8 ml Äthanol; dadurch entsteht eine Lösung, die 1·2-*n* an Salpetersäure und "80 %ig" an Alkohol ist).

[12] J. KORKISCH, P. ANTAL und F. HECHT, *J. Inorg. Nucl. Chem.* **14**, 247 (1960).
[13] J. KORKISCH und P. ANTAL, *Z. Anal. Chem.* im Druck.
[14] J. KORKISCH und A. FARAG, *Z. Anal. Chem.* **165**, 6 (1959).

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analoge Bestimmung der Verteilungskoeffizienten des Titans konnte in diesen salpetersauren alkoholischen Lösungen nicht durchgeführt werden, da teilweise Hydrolyse des Titannitrats eintrat.

Aus dieser Abb. geht hervor, dass nur das Thorium bei Änderungen der Säure- bzw. der Alkoholkonzentrationen seinen Adsorptionskoeffizienten ändert, während

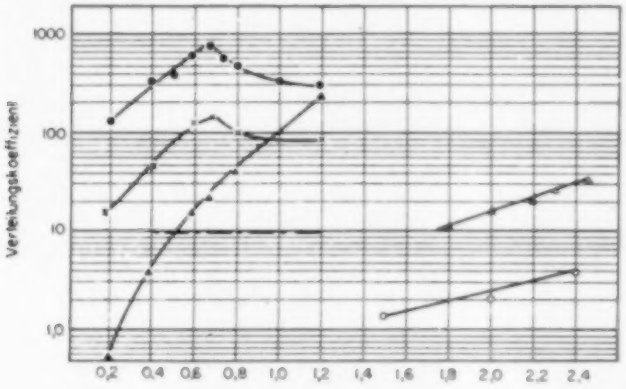

Abb. 1.—● Thorium in "80 %igem Alkohol".
× Thorium in "60 %igem Alkohol".
▲ Thorium in "40 %igem Alkohol".
△ Thorium (Danon).
○ Thorium (Carswell).
— · — · — Zirkonium in "80% igem Alkohol".

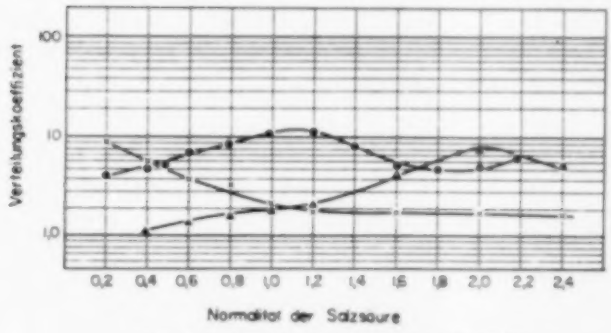

Abb. 2.—● Thorium in "80% igem Alkohol".
× Zirkonium in "80% igem Alkohol".
▲ Titan in "80% igem Alkohol".

der des Zirkoniums konstant bleibt. Es kann daher eine Trennung des Thoriums von Zirkonium und Uran (s.I. Mitteilung[12]) leicht durchgeführt werden.

In der Abb. 2 sind die Ergebnisse der in salzsauren alkoholischen Lösungen ausgeführten Bestimmungen der Verteilungskoeffizienten des Thoriums, Titans und Zirkoniums in "80 %igem Alkohol" wiedergegeben.

Wie daraus ersichtlich haben die Adsorptionskoeffizienten für alle 3 Elemente sehr kleine Werte, woraus hervorgeht, dass die Anwesenheit von Alkohol zum

Unterschied gegen Uran[12] praktisch nur einen sehr geringen Einfluss auf den an und für sich schon sehr schwachen anionischen Charakter dieser Elemente ausübt. Daraus geht hervor, dass diese Elemente auch in alkoholischer salzsaurer Lösung leicht vom Uran abtrennbar sind (vgl. I. Mitteilung[12]).

In Abb. 3 schliesslich sind unsere Ergebnisse bezüglich der in schwefelsauren alkoholischen Lösungen ermittelten Verteilungskoeffizienten des Thoriums und

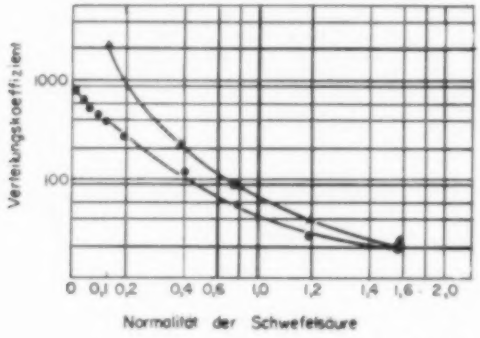

ABB. 3.—● Thorium in "80% igem Alkohol".
▲ Titan in "80% igem Alkohol".

Titans dargestellt. Diejenigen von Zirkonium konnten nicht bestimmt werden, da bei Zugabe von Alkohol Hydrolyse eintrat (bei Zusatz der gleichen Menge Wasser wird dagegen das Zirkoniumsulfat nicht hydrolysiert).

Abschliessend kann gesagt werden, dass von den 3 untersuchten Elementen Thorium, Zirkonium und Titan bei geringen Aciditäten an erster Stelle das Thorium anionischen Charakter zeigt. Hingegen weisen Zirkonium und Titan je nach der Art der angewendeten Säure entweder einen konstanten Verteilungskoeffizienten auf oder dieser ist dem des Thoriums ähnlich.

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J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 255 to 261. Pergamon Press Ltd. Printed in Northern Ireland

DINONYL NAPHTHALENE SULPHONIC ACID AS A LIQUID CATION-EXCHANGER FOR COMPLEX STUDIES*

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Abstract—The extraction of Co(II), Zn(II), Mn(II), Fe(III) and In(III) into heptane containing dinonyl naphthalene sulphonic acid, HD, from aqueous perchloric acid solutions, has been investigated, using the radioactive tracer technique. The distribution coefficients for M(II) and M(III) are inversely second power and third power, respectively, dependent upon the hydrogen ion concentration in the aqueous phase, and directly first power dependent upon the HD concentration in the heptane phase.

The formation constants of In(III) complexes of glycolate, bioxalate and Co(II) complexes of bioxalate have been determined by use of HD in heptane as a liquid cation-exchanger. For Co(II)–bioxalate, it has been demonstrated that the formation constants agree with values obtained by using resinous cation-exchanger. Since the use of liquid ion-exchanger enables one to analyse both the aqueous and non-aqueous phases, whereas in resinous cation-exchange experiments it is not convenient to analyse the non-aqueous phase, it is of decided advantage to demonstrate that the liquid ion-exchanger can be used for complex studies.

BOYD and LINDENBAUM[1] have shown that solutions of dinonyl naphthalene sulphonic acid, of di-2-ethyl hexyl phosphoric acid, of dimethyl didodecenyl ammonium chloride, and of tri-n-octylamine in nonpolar organic liquids serve as analogues of crosslinked resinous strong- and weak-acid cation-exchangers and the strong- and weak-base anion-exchangers, respectively. These liquid ion-exchangers offer several advantages over the resinous ion-exchangers: they can be used for studies of equilibria in concentrated electrolyte solutions without Donnan penetration of the exchanger phase; the rates of exchange appear to be more rapid; and the measurements of physical properties and analysis of the exchangers are more conveniently performed than with resinous exchangers. It was the purpose of this investigation to study the behaviour of dinonyl napthalene sulphonic acid as a liquid ion-exchanger and the use of this compound to determine the formation constants of several metal complexes. For comparison, the formation constants of the indium complexes were also determined by a pH method.

EXPERIMENTAL

Materials. High activity ^{60}Co, ^{54}Mn, ^{59}Fe, ^{114}In and carrier-free ^{65}Zn were obtained from Oak Ridge National Laboratory in the form of chlorides, each in HCl solution. Since chloride ion itself is a complexing agent, the metal solutions were rendered free of Cl^- by five extractions with heptane containing 10^{-3} F dinonyl naphthalene sulphonic acid and back-extraction with 0·4 M aqueous $HClO_4$. Dinonyl naphthalene sulphonic acid, hereafter referred to as HD, was obtained as a 48·6 per cent solution in n-heptane from R. T. VANDERBILT Co., Inc., and King Organic Chemicals, Inc., as a gift. The supplier stated that HD is a mixture of isomers resulting from the sulphonation of

* The work reported here was supported by the U.S. Atomic Energy Commission through Contract No. AT (30-1)-1922.

[1] G. G. BOYD and S. LINDENBAUM, Abstract I, p. 18. 134th Meeting, Amer. Chem. Soc., Chicago, Illinois, September (1958).

dinonyl naphthalene, which in turn is made by the controlled alkylation of naphthalene with nonene. HD is a monobasic acid soluble in organic solvents and only sparingly soluble in water. Its stock solution was analysed by the extraction of a known volume of the solution in heptane with standard KOH, followed by titration of an aliquot of the aqueous phase with standard HCl. The n-heptane was distilled before use. Indium metal of 99·93 per cent purity was obtained from King Products Co. All other chemicals were of C. P. grade.

Procedure. In liquid ion-exchange experiments, the aqueous phase normally was prepared to contain (a) the metal radioisotope in concentrations of the order of 10^{-6} M, (b) the complexing agent if any, in varying concentrations and (c) varying concentrations of $HClO_4$ in order to obtain the desired hydrogen ion concentration. The heptane phase contained HD in concentrations of the order of 10^{-3}–10^{-4} formula weight per litre, and was previously shaken overnight on an electric shaking machine with an equal volume of 0·1 M perchloric acid. Equal volumes of aqueous and organic phases were then mixed in glass-stoppered Erlenmeyer flasks, shaken at 25 ± 0·5 overnight, and allowed to settle for 1 hr at 25°. Aliquots of both phases were removed, and the activity of the metal ion in both phases was measured with a γ-ray scintillation counter. It was found that material balances were normally better than 98 per cent. The precision attained in distribution coefficients was generally better than ± 2 per cent.

For pH measurements, a stock solution of indium perchlorate was prepared from indium metal. The metal dissolves very slowly in hot concentrated perchloric acid, and a considerable amount of chloride ion is formed. The presence of platinum accelerates the solution, but results in contamination by Pt(IV) since a soluble Pt–In alloy is formed.[2] Therefore, the metal was dissolved in concentrated nitric acid and evaporated to near dryness with added perchloric acid five times.[3] The molarity of the indium was determined gravimetrically by precipitation with ammonium hydroxide followed by ignition at 1000°. Titration of indium perchlorate in excess perchloric acid with standard alkali to a phenolphthalein end point results in the determination of total perchlorate (C). The hydrogen ion concentration was taken to be the difference between (C) and three (In^{3+}), where (In^{3+}) is the concentration of indium ion as determined gravimetrically. The pH was measured with a Beckman pH meter, Model G with external electrodes. Solutions were maintained at 25 ± 0·5 and nitrogen gas was bubbled through the solution.

RESULTS AND DISCUSSION

From Figs. 1, 2, 3 and 4 it is seen that the distribution coefficients for M(II) and M(III) are inversely second power and third power, respectively, dependent upon the hydrogen ion concentration in the aqueous phase, and directly first power dependent upon the HD concentration in the heptane phase. The distribution coefficient, K_d, of a specific radio-nuclide is defined as the concentration of nuclide in the organic phase divided by the concentration of nuclide in the aqueous phase.

KAUFMAN and SINGLETERRY[4] have demonstrated, by the fluorescence depolarization method, micelle formation by dinonyl naphthalene sulphonates in moist benzene, and it may be inferred from this that HD in moist heptane may also exist as polymer, $(HD)_x$. An attractive explanation of the extraction of M(II)and M(III) by HD would be the following:

$$M_A^{+b} + (HD)_{xO} = M(H_{x-b}D_x)_O + bH_A^+ \quad (1)$$

where the subscripts A and O denote the aqueous and organic phases, respectively. The corresponding mass law expression, in terms of concentrations rather than activities, is:

$$\frac{[M(H_{x-b}D_x)]_O}{[M^{+b}]_A} = K\frac{[(HD)_x]_O}{[H^+]^b_A} \quad (2)$$

[2] G. A. BRUNS and D. N. HUME, *J. Amer. Chem. Soc.* **79**, 2704 (1957).
[3] G. BIEDERMANN, *Arkiv. Kemi* **9**, 279 (1956).
[4] S. KAUFMAN and C. R. SINGLETERRY, *J. Colloid Sci.* **10**, 139 (1955).

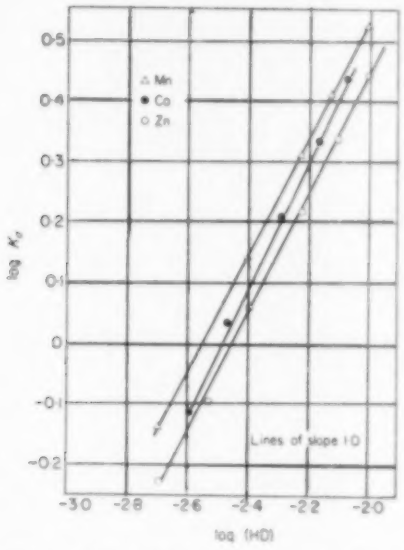

FIG. 1.—HD concentration dependency of the extraction of Mn, Co, Zn into heptane phase from 0·10 M aqueous $HClO_4$.

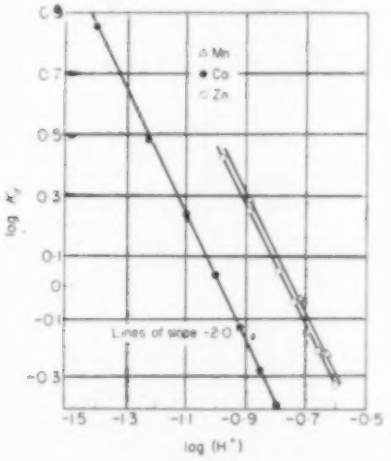

FIG. 2.—Hydrogen ion dependency of the extraction of Mn, Co, Zn into heptane phase containing HD, from aqueous $HClO_4$. For Mn and Zn, HD = 0·01 F; for Co, HD = 0·0034 F.

If M^{+b} is the only M species of importance in the aqueous phase, then the ratio $[M(H_{x-b}D_x)]_O/[M^{+b}]_A$ may be replaced by the distribution coefficient, K_d, to yield

$$K_d = K\frac{[(HD)_x]_O}{[H^+]^b_A} \tag{3}$$

It is to be noted that the HD dependency is first power, regardless of the value of b in M^{+b}. The HD dependency and acid dependency data of Figs. 1–4 for M(II) and

M(III) thus fit expression (3). This treatment is the same as that used by PEPPARD *et al.*,[8] for the extraction of M^{+b} by mono (2-ethyl hexyl) phosphoric acid.

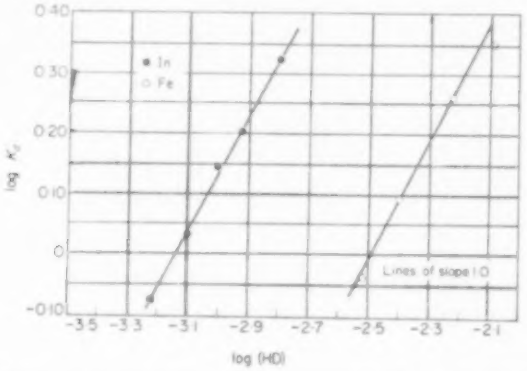

FIG. 3.—HD concentration dependency of the extraction of Fe(III) and In(III) into heptane phase from 0·40 and 0·30 M aqueous $HClO_4$, respectively.

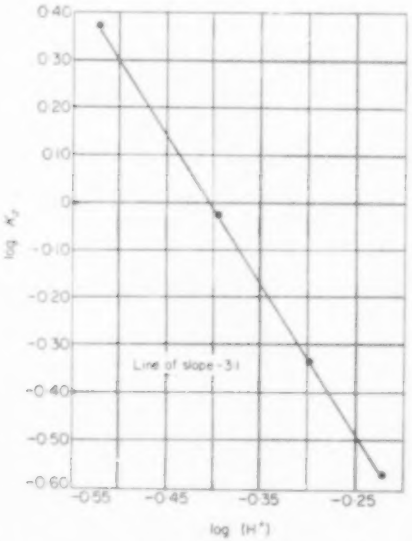

FIG. 4.—Hydrogen ion concentration dependency of the extraction of Fe(III) into heptane containing 0·0034 F HD from aqueous $HClO_4$.

Equation (3) may be rearranged to give

$$\frac{K}{x} = K_d \frac{[H^+]^b_A}{(HD)_O} \tag{4}$$

where $(HD)_O$ means the *formality* of the extractant $(HD)_x$, not the molarity of monomeric HD. The average values of K/x obtained from the data of Figs. 1–4 for the various metal ions are listed in Table 1.

[8] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* 7, 276 (1958).

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K/x thus is equal to three for the three divalent metal ions reported and is somewhat higher for the trivalent metal ions. If one assumes that x does not vary appreciably, the dependence of the magnitude of K/x on the charge of the metal ion is completely reasonable. It must be mentioned that while the average x has a discrete value under the experimental conditions of Figs. 1–4, it may have a different discrete value under a different set of conditions.

TABLE 1.—VALUES OF K/x FOR M(II) AND M(III) FROM THE DATA OF FIGS. 1–4

	Zn(II)	Co(II)	Mn(II)	Fe(III)	In(III)
K/x	2·9	3·2	3·3	20·4	35·1

In order to investigate the use of HD as a liquid cation-exchanger for complex studies, we chose initially the indium glycolate system and, for comparison purpose, we also carried out a pH study of this system. In the presence and absence of a ligand A^-, in the aqueous phase the distribution coefficients may be written

$$K_d = \frac{(M)_o}{(M)_a + (MA)_a + (MA_2)_a + \ldots} \tag{5}$$

$$K^\circ_d = \frac{(M)_o}{(M)_a} \tag{6}$$

respectively. Dividing equation (6) by equation (5), and introducing the formation constant k_i, where $k_i = (MA_i)/(MA_{i-1})(A)$, one can obtain

$$\frac{K^\circ_d}{K_d} = \frac{(M) + (MA) + (MA_2) + \ldots}{(M)} \tag{7}$$

$$= 1 + k_1(A) + k_1k_2(A)^2 + \ldots \tag{8}$$

If only a 1 : 1 complex exists, then $1/K_d$ will vary linearly with (A^-) and the slope is equal to k_1/K°_d, from which value of k_1 can be calculated. In the case that a 1 : 2 complex also exists, equation (8) rearranges to

$$y = \frac{(K^\circ_d/K_d) - 1}{(A)} = k_1 + k_1k_2(A) \tag{9}$$

so that the values of k_1 and k_2 can be obtained from the intercept and slope of a linear y vs. (A) plot. The treatment outlined here is analogous to that for a resinous cation-exchanger, Dowex-50, for complex studies.[6] A similar treatment is presented by DAY and STOUGHTON[7].

Fig. 5 shows the liquid ion-exchange results obtained when the heptane phase containing $1{\cdot}47 \times 10^{-3}$ F HD is equilibrated with an aqueous phase containing 0·30 M $HClO_4$ and 0·2–0·6 M glycolic acid. The value of $1/K_d$ extrapolated to $(A^-) = 0$ agrees with the value of $1/K^\circ_d$ determined directly. From the slope of the line, k_1 of the In(III)–glycolate complex is calculated to be 3·15 ($\mu = 0{\cdot}30$).

[6] J. SCHUBERT, E. L. LIND, W. M. WESTFALL, R. PLLEGER and N. C. LI, *J. Amer. Chem. Soc.* **80**, 4799 (1958).
[7] R. A. DAY, JR. and R. W. STOUGHTON, *J. Amer. Chem. Soc.* **72**, 5662 (1950).

Fig. 6 summarizes the pH results for the In(III)–glycolate system. By using Bjerrum's method[8] the value of log k_1 is calculated to be 2·95 ($\mu = 0{\cdot}14$). This is in very good agreement with the liquid ion-exchange value, log $k_1 = 3{\cdot}15$ ($\mu = 0{\cdot}30$) and the EMF value, log $k_1 = 2{\cdot}93$[9] ($\mu = 1{\cdot}0$).

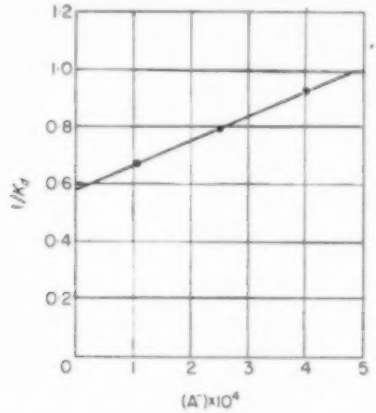

FIG. 5.—Liquid ion-exchange results for In(III) in the presence of glycolic acid, $(H^+) = 0{\cdot}30$ M at 25°C. pK of glycolic acid = 3·64.

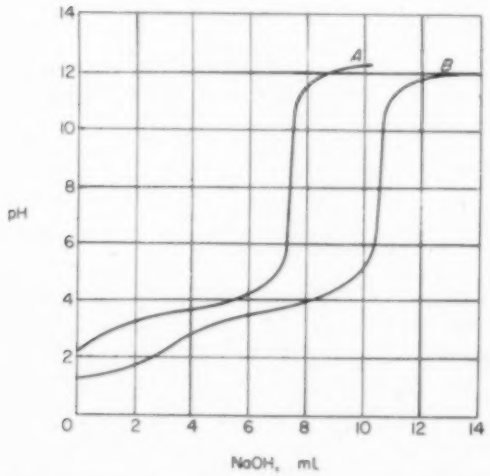

FIG. 6.—Titration of 25 ml 0·2 M glycolic acid, curve A; and in the presence of 0·01 M In(III), excess 0·0538 M $HClO_4$, curve *B*. NaOH = 0·6666 M.

AHRLAND *et al.*[10] have shown that the complex formation curve is dependent on the concentration of metal ion if polynuclear complexes exist; while the complex formation curve is independent of metal ion concentration for mononuclear complexes. The complexes of In(III) are difficult to study because the trivalent metal cation is readily hydrolysed.[3] In the liquid ion-exchange experiments, the concentration of

[8] J. BJERRUM, *Metal Ammine Formation in Aqueous Solution*. Haas, Copenhagen (1941).
[9] N. SUNDEN, *Svensk Kem. Tidskr.* **65**, 257 (1953).
[10] S. AHRLAND, *Acta Chem. Scand.* **3**, 374 (1949).

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metal ion (radioisotope) is of the order of 10^{-6} M whereas in the pH and e.m.f. experiments the concentration of metal ion is of the order of 10^{-2}–10^{-3} M. Since the formation constants obtained by these different experiments employing widely different metal ion concentrations agree with one another, we can be reasonably certain that the In(III)–glycolate complex is mononuclear and that the formation constant is valid.

In(III) complex of bioxalate was also studied by the liquid ion-exchanger method, in which 25 ml aqueous phase containing 0·30 M $HClO_4$, 10^{-6} M ^{114}In and 0·8 to

TABLE 2.—LIQUID ION-EXCHANGE EXPERIMENTS WITH Co(II) COMPLEXES OF BIOXALATE ($HC_2O_4^-$). HEPTANE CONTAINING $6{\cdot}33 \times 10^{-3}$ F HD EQUILIBRATED WITH AQUEOUS PHASE CONTAINING 0·1 M $HClO_4$, ^{60}Co AND VARYING CONCENTRATIONS OF OXALIC ACID. pK_1 OF OXALIC ACID: 1·28

$(HC_2O_4^-) = (HA^-) \times 10^2$	$1/K_d$	$\frac{(K^-_d/K_d) - 1}{(HA^-)} = y$
0	0·53	
1·05	0·80	48·4
2·90	1·46	60·5
3·70	1·89	69·4
4·25	2·17	72·6

4×10^{-3} M $H_2C_2O_4$ was equilibrated with 25 ml of heptane containing $1{\cdot}2 \times 10^{-3}$ F HD. The value of k_1 is calculated to be $1{\cdot}2 \pm 0{\cdot}1 \times 10^3$.

Co(II) complexes of bioxalate have been determined by SCHUBERT *et al.*[6]: log $k_1 = 1{\cdot}66$, log $k_2 = 1{\cdot}25$, using the resinous cation-exchanger, Dowex-50. Table 2 summarizes the results we have obtained by the liquid ion-exchanger method.

The data of Table 2 yield a linear y vs. (HA^-) plot, from which the values of the formation constants have been calculated to be: log $k_1 = 1{\cdot}61$, log $k_2 = 1{\cdot}28$. The formation constants are thus in excellent agreements with values derived from resinous cation-exchange method. Since the use of a liquid ion-exchanger in a nonpolar organic solvent allows one to analyse both the aqueous and non-aqueous phases, whereas in using resinous ion-exchanger it is inconvenient to analyse the non-aqueous phase, it would be of decided advantage to demonstrate that liquid ion-exchangers can be used for complex studies. This we have done by presenting the results with several metal complexes.

Acknowledgements—The authors are grateful to Miss J. YU for her work on In(III)–HD and In–$HC_2O_4^-$ complexes, and to Miss M. BECHTOLD for assisting with some of the experiments.

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INORGANIC SALTS DISSOLVED IN NON-AQUEOUS OR IN MIXED SOLVENTS—II

CONDUCTOMETRIC STUDIES OF $SnCl_4 \cdot 5H_2O$ DISSOLVED IN PURE METHANOL OR IN METHANOL PLUS WATER

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Abstract—Conductance data at 25°C are given for $SnCl_4 \cdot 5H_2O$ dissolved in water, methanol, or methanol–water. Empirical relations between measured values and concentration terms are illustrated. Coagulation phenomena are also reported.

SPECTROPHOTOMETRIC measurements[1] have shown that $SnCl_4 \cdot 5H_2O$ dissolved in water–methanol of fixed compositions does not obey Beer's Law. At all wavelengths and for all Sn(IV) concentrations the molar extinction coefficient decreases with increasing methanol concentration to a point where the methanol concentration is approximately 21 M and the water concentration is 7 M. Further increases in the methanol concentration, increase the molar extinction coefficient. This effect cannot be interpreted in terms of classical dielectric properties of mixed solvents, as there should be a continuous change in one direction in passing from one pure solvent through mixtures to the other. The 3 : 1 methanol : water ratio at which the minimum is found suggests that the Sn(IV) species and methanol react competitively with water. In the present work the results of a detailed conductometric study on these systems are given.

EXPERIMENTAL

Immediately before use distilled water and Fisher Spectrograde methanol were thoroughly saturated with dry nitrogen (oxygen content less than 0·01 per cent, dew point below −40 C, supplied by Albany Welding Company). Identical results were obtained with Reagent Grade $SnCl_4 \cdot 5H_2O$ supplied by Fisher (Lot no. 782698) and that from Baker and Adamson (Lot no. 90023).

Solutions of 0·1171 and 1·171 M were prepared by dissolving weighed amounts of $SnCl_4 \cdot 5H_2O$ in pure methanol or in water. Further dilution made immediately before measurements, yielded solutions of the desired Sn(IV) and solvent compositions.

Conductance measurements[2] were made with the General Radio Impedance Bridge (Type 650-P1) and a thermostated bath for the cell set at 25 ± 0·02 C. Specific gravities of the bulk (0·1171 and 1·171 M) and sample solutions were determined at 25°C after the resistance had been measured. These specific gravities were required to compute accurately the concentrations of the samples.

Reproducibility tests showed that the conductance measurements were accurate to better than 1·0 per cent. Even after 7 hr the conductance of the solutions remained unchanged. In all cases the conductance of the pure solvent was less than 0·1 per cent of the solution conductance.

The concentrations of the sample solutions were as follows: for $SnCl_4 \cdot 5H_2O$, sixteen concentrations between 0·002342 and 0·4684 mole/l. for each solvent; and for methanol–water, fourteen concentrations in the range 0·00 to 24·56 moles/l. of methanol and 55·48 to 0·00 mole/l. of water.

[1] M. M. DE MAINE and P. A. D. DE MAINE, *J. Inorg. Nucl. Chem.* **11**, 13 (1959).
[2] P. A. D. DE MAINE and E. KOUBEK, *J. Inorg. Nucl. Chem.* **11**, 329 (1959).

RESULTS

Although the molar conductance decreases as the Sn(IV) concentration increases for a fixed solvent composition, the data do not fit the simple Onsager equation (Fig. 1).

Plots of the specific conductance versus the Sn(IV) concentration for pure methanol solutions are linear in two concentration regions. As the concentration of water is increased the transition between the two linear regions becomes less well-defined

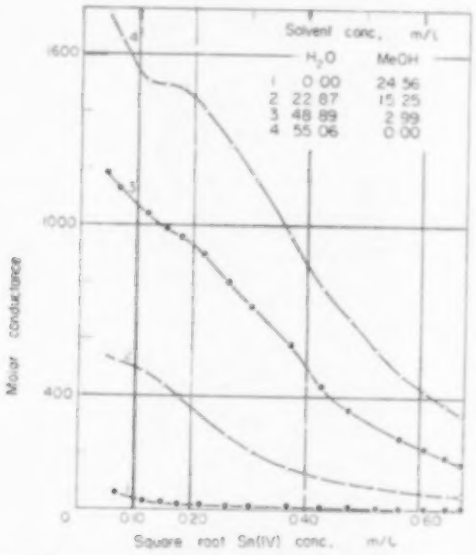

FIG. 1.—Plots of the molar conductance versus the square root of the Sn(IV) concentration in mole/l. for $SnCl_4 \cdot 5H_2O$ dissolved in methanol–water. The solvent compositions are indicated.

(Fig. 2). In Table 1 are given the slopes and positive intercepts for plots of specific conductance in the solvent indicated versus Sn(IV) concentration.

For solutions with fixed Sn(IV) concentrations, plots of molar conductance versus methanol concentration yield two well-defined straight lines if the tin concentration is below 0·0938 mole/l. (Fig. 3). For higher Sn(IV) concentrations, no such linearity is evident.

Visible coagulation occurs slowly within 0·02–10 hr after preparation for solutions with high water and low Sn(IV) concentrations. Table 2 gives the concentrations which, when exceeded, yield solutions which remain optically clear permanently. At lower concentrations, the occurrence of visible coagulation does not change significantly the resistance of the solution. In a typical example, visible coagulation was evident only 1100 sec after solution preparation, and the resistance changed from 2080 to 2070 Ω. No sudden, irregular conductance change was noted in values for a series of samples involving both "coagulating" and "non-coagulating" relative concentrations.

DISCUSSION

The coagulation phenomenon (see above) suggests that micelle formation does not involve any ionic species present in the solution; and must therefore result from

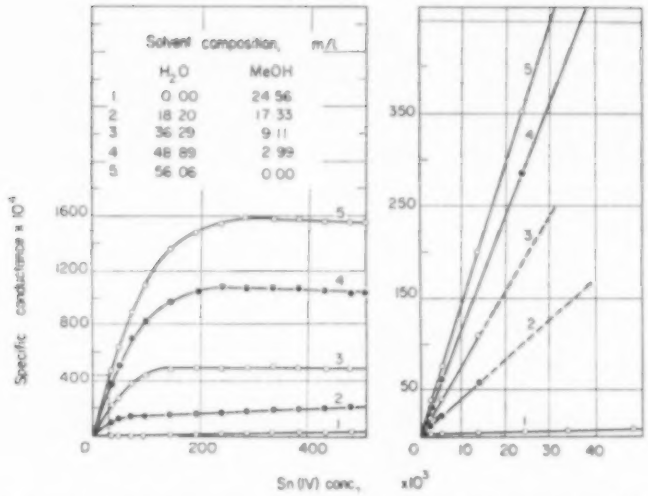

FIG. 2.—Plots of the specific conductance versus the Sn(IV) concentrations for the indicated solvent.

TABLE 1.—SLOPES AND POSITIVE INTERCEPTS FOR THE LINEAR PLOTS OF SPECIFIC CONDUCTANCE VS. Sn(IV) CONCENTRATION WITH CONSTANT SOLVENT COMPOSITION IN THE Sn(IV) CONCENTRATION REGIONS INDICATED*

MeOH conc.	H_2O conc.	Lower concentration region				Upper concentration region			
		c	*m*	Sn(IV) conc.	*p*	*c*	*m*	Sn(IV) conc.	*p*
24·56	0·00	+2·0	+0·019	0·0024 → 0·0478	6	+4·0	+0·008	0·071 → 0·470	11
22·89	4·48	+2·0	+0·172	0·0024 → 0·0334	1	+20·0	+0·014	0·071 → 0·470	6
21·12	9·04	+2·0	+0·280	0·0024 → 0·0048	2	+36·0	+0·020	0·071 → 0·470	10
19·25	13·64	+2·0	+0·324	0·0024 → 0·0232	3	+75·0	+0·019	0·071 → 0·470	10
17·33	18·20	+2·0	+0·426	0·0024 → 0·0133	3	+134	+0·018	0·141 → 0·470	8
15·25	22·87	+2·0	+0·518	0·0024 → 0·0133	3	+187	+0·023	0·141 → 0·470	8
13·20	27·31	+2·0	+0·612	0·0024 → 0·0133	3	+278	+0·022	0·141 → 0·470	8
11·17	31·80	+2·0	+0·714	0·0024 → 0·0133	3	+373	+0·025	0·141 → 0·470	8
9·11	36·29	+2·0	+0·816	0·0024 → 0·0133	3	+506	−0·002	0·188 → 0·470	7
7·06	40·73	+2·0	+0·947	0·0024 → 0·0133	3	+675	−0·008	0·188 → 0·470	7
5·01	44·72	+2·0	+1·100	0·0024 → 0·0133	3	+841	−0·001	0·188 → 0·470	7
2·99	48·89	+2·0	+1·223	0·0024 → 0·0232	3	+1135	−0·015	0·234 → 0·470	6
0·99	52·94	+2·0	+1·383	0·0024 → 0·0232	3	+1542	−0·037	0·282 → 0·470	5
0·00	55·06	+2·0	+1·523	0·0024 → 0·0232	3	+1650	−0·018	0·282 → 0·470	5

* *m* and *c* are the slopes (mho cm^{-1} l./mole) and positive intercepts (mho cm^{-1}) respectively. *p* is the number of points defining the linear region. All concentrations are mole/l.

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polymerization of covalent species already present in the solution before visible coagulation occurs. Since visible coagulation is not accompanied by a measurable change in the resistance of the solutions, removal of these covalent species from solution must not significantly disturb the equilibrium between ionic and covalent species of Sn(IV). This indicates that the Sn(IV) must be extensively hydrolysed in dilute solutions with high water concentrations. The high values found for the molar

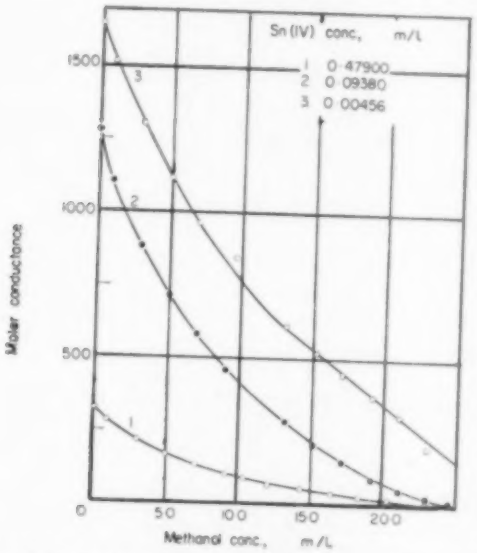

FIG. 3.—Plots of the molar conductance for solutions with fixed Sn(IV) concentrations as indicated versus the methanol concentration.

conductance of these solutions (Table 3) supports this view. Our calculations show that the 0·00234 molar solution in water must be completely hydrolysed.*

As increased methanol concentrations prevent coagulation (Table 2) and decrease the molar conductance (Table 3) for dilute Sn(IV) solutions, the methanol must interact specifically with covalent and ionic species of Sn(IV).

The form of the plots for molar conductance versus the square root of the Sn(IV) concentration, with solvent composition constant (Fig. 1), indicates that hydrolysis decreases rapidly as the methanol or Sn(IV) concentration is increased. The comparatively linear regions of these plots suggests that for high concentrations of Sn(IV) and methanol the normal ionization processes predominate. Our calculations show that some hydrolysis must also occur in solutions with high water concentration for high Sn(IV) concentration,† in which visible coagulation does not occur. Similar calculations indicate that the low molar conductance for solutions with low water concentrations is probably due entirely to ionization of the halide, with negligible hydrolysis or alcoholysis.

* With the assumption that the hydrolysis occurs thus: $SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4Cl^- + 4H^+$, the predicted molar conductance is 1704·7 mho cm^{-1} l./mole and the experimental value is 1747·0.

† In a typical calculation we have assumed the limiting ion conductance for Sn^{+4} is 250. Complete ionization with no hydrolysis would give a molar conductance of less than 554 mho cm^{-1} l./mole. A 0·282 M solution had molar conductance near 570 and at lower concentrations very much larger values were found.

TABLE 2.—MINIMUM $SnCl_4 \cdot 5H_2O$ CONCENTRATIONS FOR SELECTED WATER–METHANOL COMPOSITIONS AT WHICH VISIBLE COAGULATION APPEARED*

MeOH	Water	$SnCl_4 \cdot 5H_2O$	Coagulation time (sec)
24·56	0·00	—	
22·89	4·48	—	coagulation was
21·12	9·04	—	never observed.
19·25	13·64	—	
17·33	18·20	0·00484	more than 2000
15·25	22·87	0·00485	more than 1000
13·20	27·31	0·01450	more than 12000
11·17	31·80	0·01450	more than 1000
9·11	36·29	0·01450	about 850
5·01	44·72	0·0237	more than 12000
2·99	48·89	0·0236	more than 8000
0·99	52·94	0·0328	more than 36000
0·00	55·06	0·0327	less than 1000

* "Coagulation time" is the period between mixing and the first observation of visible turbidity. Concentrations in mole/l.

TABLE 3.—MOLAR CONDUCTANCE FOR DILUTE SOLUTIONS OF Sn(IV) DISSOLVED IN METHANOL–WATER CONCENTRATIONS OF Sn(IV), METHANOL AND WATER ARE GIVEN

Tin(IV) conc. (mole/l.)		Molar conductance						
MeOH conc. (mole/l.)	H_2O conc. (mole/l.)	0·00242	0·00484	0·0145	0·0241	0·0338	0·0484	0·0725
24·56	0·00	—	61·4	32·0	23·9	23·3	17·3	14·6
22·89	4·48	—	206	99·9	63·5	—	52·3	34·6
21·12	9·04	355	318	215	164	124	95	72
19·25	13·64	420	379	316	256	208	176	122
17·33	18·20	474	463	401	354	307	250	189
15·25	22·87	549	524	489	441	400	282	264
13·20	27·31	—	621	562	529	493	430	348
11·17	31·80	681	723	666	619	585	530	441
9·11	36·29	808	853	760	731	648	609	538
7·06	40·73	1000	971	891	855	838	759	665
5·01	44·72	1189	1133	1046	992	964	902	803
2·99	48·89	1594	1312	—	1294	1294	1155	1101
0·99	52·94	—	1526	1460	1393	1347	1273	1176
0·00	55·06	1747	1660	1548	1512	1491	1372	1295

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A reaction scheme may be:

$$\text{Sn(IV) halide} + \text{methanol} \rightleftharpoons \text{un-ionized complex} \quad \text{(A)}$$

$$\text{Sn(IV) halide} + \text{water} \rightleftharpoons \text{un-ionized complex} \rightleftharpoons \text{hydrolysis products} \rightleftharpoons \text{ions} \quad \text{(B)}$$

Process (A) may also have an ionization step, but if so, the ionization must be very much less than that for process (B). Maximum concentrations of hydrolysis products are determined by the solubility products for the basic salts and hydroxides formed. Thus the almost complete hydrolysis for low Sn(IV) concentrations in water and the rapid decrease on addition of methanol or more Sn(IV) can be understood.

While no detailed mathematical analysis of the spectrophotometric[1] and conductance data can be attempted because of the complexity of the system, competing reactions (A) and (B) do qualitatively explain the minima reported for the spectrophotometric data[1] (also see Introduction) and the monotonic decreasing dependence of molar conductance on methanol concentration (Fig. 3) for solutions with fixed Sn(IV) concentrations. It may also be shown that reaction schemes which assume no specific interactions, cannot explain these data.

Acknowledgements—Sincere thanks are due the Research Corporation and the Research Foundation, State University of New York for financial support of this work. The author also acknowledges gratefully technical assistance by G. E. McAlonie.

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INORGANIC SALTS DISSOLVED IN NON-AQUEOUS OR IN MIXED SOLVENTS—III

CONDUCTANCE STUDIES OF $SnCl_4 \cdot 5H_2O$ AND $SnCl_2 \cdot 2H_2O$ DISSOLVED SEPARATELY IN METHANOL–CARBON TETRACHLORIDE

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(*Received* 12 *August* 1959; *in revised form* 5 *October* 1959)

Abstract—Conductance measurements are reported for $SnCl_4 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$ dissolved separately in methanol and in methanol–carbon tetrachloride at 25°C. Empirical relations between the specific conductance and the Sn(IV) and Sn(II) concentrations are given. Phase separation phenomena for the separate salts in the mixed solvent are also reported. Mechanisms which qualitatively explain the data are discussed.

DE MAINE and DE MAINE[1] reported that $SnCl_4 \cdot 5H_2O$ dissolved in methanol or in methanol–carbon tetrachloride obeys Beer's Law for any fixed solvent composition. The molar extinction coefficient of the Sn(IV) species varies with the methanol concentration. This suggests that specific interaction occurs between a mononuclear Sn(IV) species and the methanol.

These authors also reported that $SnCl_2 \cdot 2H_2O$ in the same solvents does not obey Beer's Law for any single fixed solvent composition. However, the molar extinction coefficients do not change as the solvent composition is varied. Thus it seems that two mononuclear Sn(II) species interact specifically to form a weak complex. As the deviations from Beer's Law become less marked when the methanol concentration is decreased[1] at least one of the interacting mononuclear Sn(II) species must be an ion.

In the same work[1] it was reported that for certain critical concentrations of $SnCl_4 \cdot 5H_2O$, methanol, and carbon tetrachloride two-layer formation was observed. In such systems clear single-layer solutions were obtained by increasing the methanol concentration.

In the present work we report results for a detailed conductometric study of the two tin salts dissolved separately in methanol or in methanol–carbon tetrachloride at 25°C.

EXPERIMENTAL

Fisher Spectro Grade methanol and carbon tetrachloride were thoroughly purged with dry nitrogen (dew point less than −40°C; oxygen less than 0·01 per cent), supplied by Albany Welding Company. Fisher reagent grade $SnCl_4 \cdot 5H_2O$ (lot no. 782698) and $SnCl_2 \cdot 2H_2O$ (lot no. 1311) were purged with dry nitrogen to remove traces of oxygen.

Bulk solutions were made by accurately weighing the desired quantity of salt and dissolving it in pure methanol in a dry nitrogen atmosphere.[2] These solutions were diluted to the desired concentrations immediately before measurements were made. Solution preparation and the filling of the conductivity cells, were performed in a dry nitrogen atmosphere.

[1] M. M. DE MAINE and P. A. D. DE MAINE, *J. Inorg. Nucl. Chem.* **11**, 13 (1959).
[2] P. A. D. DE MAINE and E. KOUBEK, *J. Inorg. Nucl. Chem.* **11**, 329 (1959).

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Conductance measurements were made with the General Radio Impedance Bridge (Type 650–P1) and a Leeds and Northrup type cell immersed in a thermostat set at 25 ± 0·02°C. Reproducibility tests showed that the measured values are accurate to better than one per cent; and the resistance of the solutions showed no measurable change even after 1 hr.

Specific gravities of the solutions were determined at 25°C immediately after the conductivity measurements were made. These values were required for accurate calculation of the concentrations.

The solutions studies were as follows: for $SnCl_4 \cdot 5H_2O$, sixteen salt concentrations between 0·0023 and 0·468 mole/l. for each of ten solvent compositions (methanol from 24·56 to near 6·00 moles/l. with CCl_4 as diluent).

For $SnCl_2 \cdot 2H_2O$; sixteen salt concentrations between 0·0026 and 0·520 mole/l. for each of thirteen solvent compositions (methanol varied from 24·56 to 0·69 mole/l. with CCl_4 as diluent).

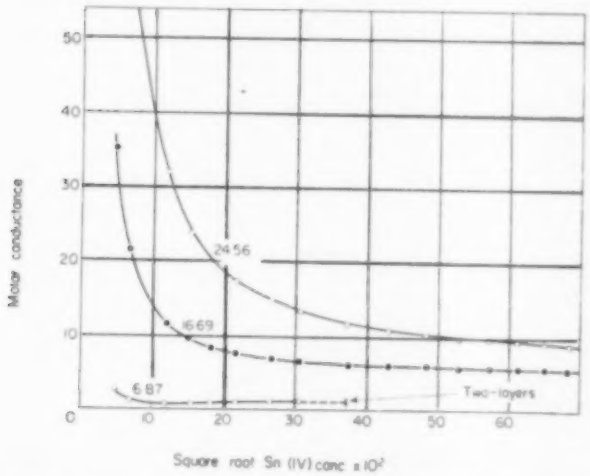

FIG. 1.—Plots of molar conductance versus the square root of the Sn(IV) concentrations for $SnCl_4 \cdot 5H_2O$ dissolved in methanol–carbon tetrachloride at the indicated methanol concentrations. All concentrations are in mole/l.

RESULTS

Solutions with $SnCl_4 \cdot 5H_2O$ *dissolved in methanol or in methanol–carbon tetrachloride*

Plots of the molar conductance versus the square root of the Sn(IV) concentration at constant solvent compositions are linear for high Sn(IV) concentrations. The salt concentration range for which linearity is evident increases with increased methanol concentration, and the molar conductance decreases. The slopes of these linear portions simultaneously progress from negative to positive values. Fig. 1 illustrates these points.

Plots of the specific conductance versus the Sn(IV) concentration for solutions of fixed solvent composition, show well-defined linearity for two ranges of salt concentration. As the methanol concentration is decreased the specific conductance and the slopes of the lines decrease. These points are illustrated in Fig. 2. Slopes and positive intercepts for the linear plots at the indicated salt concentration region, together with the number of points with root-mean square deviations from the line of less than one per cent, are given in Table 1.

In agreement with published work[1] two-layer formation occurs for certain critical methanol and salt concentrations (Fig. 2). No deviations from the linear

relations just described were observed for any solvent mixture until two-layer formation had actually taken place. A detailed conductometric and analytical study of two phase systems is in progress.[3]

Plots of the molar conductance versus the methanol concentration, at constant Sn(IV) concentrations, yield hyperbolic curves whose pitch gradually decreases as the Sn(IV) concentration increases. Similar plots for the specific conductance data yielded hyperbolic curves at Sn(IV) concentrations less than 0·1800 mole/l., and straight lines at higher concentrations.

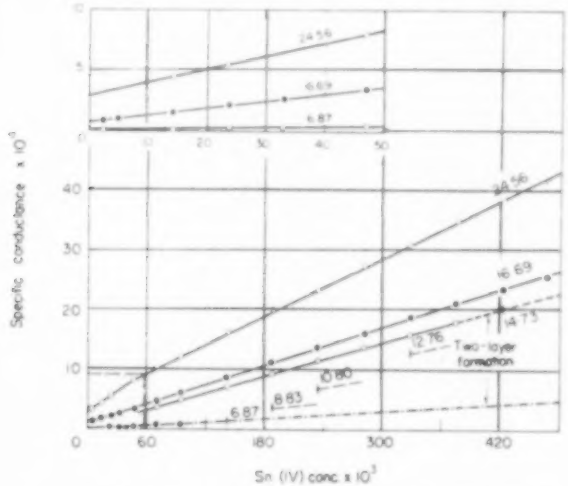

FIG. 2.—Plots of specific conductance versus the Sn(IV) concentration for $SnCl_4 \cdot 5H_2O$ dissolved in methanol–carbon tetrachloride at indicated methanol concentrations. Broken lines indicate regions where two-layer formation was observed. Relations for solutions with low Sn(IV) concentrations are illustrated in the inset. All concentrations are in mole/l.

Solutions with $SnCl_2 \cdot 2H_2O$ *dissolved in methanol or in methanol–carbon tetrachloride*

Plots of the molar conductance versus the square root of the Sn(II) concentration at fixed solvent compositions again show straight line portions at high salt concentrations. The $SnCl_2 \cdot 2H_2O$ concentration for which linearity is evident decreases as the methanol concentration is increased. Slopes for the straight line portions again gradually increase from negative to positive as the methanol concentration is decreased, but the transition is more marked than for the solutions with $SnCl_4 \cdot 5H_2O$.

Plots of the specific conductance versus Sn(II) concentrations at constant solvent compositions are linear for two salt concentration regions and intersect at a sharp transition point. As the methanol concentration is decreased the specific conductance and the slopes for both intersecting straight lines also decrease. However, the concentration ordinate, which describes the transition point, remains unaltered with methanol concentration. In Table 2 are given the slopes, one intercept, the concentration regions, and the number of points with root-mean-square deviations less than 1 per cent for the intersecting straight lines. Co-ordinates for the sharp transition points are also given.

[3] P. A. D. DE MAINE. In preparation.

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TABLE 1.—THE SLOPE, m, (mho cm^{-1} l./mole) AND THE SPECIFIC CONDUCTANCE AXIS INTERCEPT, c, (mho cm^{-1}) FOR THE LINEAR RELATIONS BETWEEN SPECIFIC CONDUCTANCE AND $SnCl_4 \cdot 5H_2O$ CONCENTRATION FOR THE INDICATED MIXED SOLVENTS. THE NUMBER OF POINTS (p) WITH ROOT-MEAN SQUARE DEVIATIONS LESS THAN 1 PER CENT IN THE INDICATED SALT CONCENTRATION REGIONS ARE ALSO GIVEN. ALL CONCENTRATIONS ARE IN mole/l.

MeOH conc.	Low concentrations				High concentrations			
	$m \times 10^2$	$c \times 10^4$	Salt conc. range $\times 10^3$	p	$m \times 10^2$	$c \times 10^4$	Salt conc. range $\times 10^3$	p
24·56	1·26	4·10	4·0 → 50·0	4	0·81	4·40	40·0 → 500·0	11
22·59	0·90	2·30	5·0 → 50·0	4	0·75	3·00	20·0 → 500·0	11
20·62	0·74	1·90	5·0 → 50·0	4	0·71	1·90	10·0 → 500·0	11
18·66	0·69	1·05	4·0 → 50·0	5	0·62	1·30	10·0 → 500·0	14
16·69	0·54	0·80	0·0 → 50·0	6	0·54	1·00	10·0 → 500·0	14
14·73	0·48	0·50	0·0 → 50·0	6	0·49	0·42	0·0 → 450·0	14
12·77	0·34	0·25	0·0 → 50·0	6	0·38	0·20	5·0 → 350·0	10
10·80	0·24	0·10	0·0 → 50·0	6	0·28	0·00	5·0 → 255·0	8
8·84	0·15	0·05	0·0 → 50·0	6	0·20	0·00	15·0 → 200·0	6
6·87	0·08	0·00	0·0 → 50·0	6	0·10	0·00	15·0 → 100·0	5

TABLE 2.—THE SLOPES, m, (mho cm^{-1} l./mole) AND THE SPECIFIC CONDUCTANCE AXIS INTERCEPT, c, (mho cm^{-1}) FOR THE LINEAR RELATIONS BETWEEN SPECIFIC CONDUCTANCE AND $SnCl_4 \cdot 2H_2O$ CONCENTRATION FOR THE INDICATED MIXED SOLVENT. THE NUMBER OF POINTS (p) WITH ROOT-MEAN SQUARE DEVIATIONS LESS THAN 1 PER CENT IN THE INDICATED SALT CONCENTRATION REGIONS ARE ALSO GIVEN. Z AND z ARE CONCENTRATION AND SPECIFIC CONDUCTANCE CO-ORDINATES FOR THE TRANSITION POINT, OBTAINED BY SIMULTANEOUS SOLUTION OF THE TWO LINEAR FUNCTIONS. ALL CONCENTRATIONS ARE IN mole/l.

MeOH conc.	Low salt concentrations				High salt concentrations				$Z \times 10^3$	$z \times 10^4$
	$m \times 10^2$	$c \times 10^4$	Salt conc. range $\times 10^3$	p	$m \times 10^2$	$c \times 10^4$	Salt conc. range $\times 10^3$	p		
24·56	0·54	1·18	15·0 → 210·0	8	0·59	0·70	150·0 → 520·0	8	97·9	6·51
22·59	0·49	0·66	15·0 → 210·0	8	0·52	0·10	150·0 → 520·0	8	175·0	9·03
20·62	0·40	0·72	15·0 → 210·0	9	0·50	−1·10	150·0 → 520·0	8	187·6	8·20
18·66	0·36	0·56	15·0 → 210·0	8	0·45	−1·40	150·0 → 520·0	8	222·7	8·58
16·69	0·31	0·47	5·0 → 210·0	9	0·43	−2·35	200·0 → 520·0	6	243·1	8·01
14·73	0·26	0·32	5·0 → 210·0	8	0·40	−2·30	200·0 → 520·0	7	192·6	5·33
12·77	0·22	0·18	0·0 → 210·0	11	0·35	−2·41	200·0 → 520·0	7	194·7	4·46
10·80	0·15	0·10	0·0 → 210·0	10	0·33	−3·30	200·0 → 520·0	7	194·3	3·01
8·84	0·11	0·10	0·0 → 110·0	8	0·29	−3·80	250·0 → 520·0	5	213·1	2·44
6·87	0·06	0·00	0·0 → 110·0	5	0·22	−3·40	300·0 → 400·0	2	212·2	1·49
4·91	0·01	0·00	0·0 → 210·0	7	—	—	—	—	—	—

Plots of the specific conductance versus the methanol concentration for constant salt concentrations are also linear at salt concentrations greater than 0·210 moles/l. For Sn(II) concentrations below 0·210 moles/l. the plots show a positive curvature. Plots for the molar conductance have the same general characteristics as those for $SnCl_4 \cdot 5H_2O$ solutions.

Two-layer formation was first observed for a solution 0·260 mole/l. in $SnCl_2 \cdot 2H_2O$ and 6·00 moles/l. in methanol. No two-layer formation was observed for any Sn(II) solutions containing 6·89 moles/l. of methanol. Thus the phenomenon of two-layer formation occurs at much higher methanol concentrations for Sn(IV) (Fig. 2).

DISCUSSION

A detailed theoretical examination of the conductometric and spectrophotometric data for tin chloride systems is now in progress and will be submitted separately.[4] At present only general conclusions about these systems will be drawn.

Solutions with $SnCl_4 \cdot 5H_2O$

The linear portions of plots of the molar conductance versus the square root of the Sn(IV) concentration, at fixed solvent composition (Fig. 1), suggest that for the high salt concentrations a single ionization process predominates. For lower salt concentrations two or more ionization processes, which may be consecutive or competitive, must be operative. Since the linear portions extend to lower salt concentrations as the methanol concentration is lowered (Fig. 1), the number of competing or separate ionization processes is reduced at decreased methanol concentrations. From specific conductance versus Sn(IV) concentration plots (Fig. 2, Table 1), it appears that one ionization process predominates at methanol concentrations below 20·62 moles/l., in which region the plots are single straight lines.

The gradual decrease in values for the molar conductance as the methanol concentration is decreased, fits the accepted view of the role played by the average dielectric constant of the solvent.

Solutions with $SnCl_2 \cdot 2H_2O$

The linear sections of plots of the molar conductance versus the square root of the Sn(II) concentration for fixed solvent composition, suggest predominance at high salt concentrations of a single ionization process with formation of only two ions. For low salt concentrations two or more ionization processes, which may be successive or competitive, are operative. At decreased methanol concentrations no single process predominates as is the case of Sn(IV) solutions (evidence from Table 2). As the concentration co-ordinate for the point of intersection of the two straight lines appears to be nearly independent of the methanol concentration for the mixed solvents (Table 2), it seems that only one ionization process is operative in each concentration region, and that the salt concentration alone determines which of the two ionization processes is operative.

Acknowledgements—The authors desire to thank the Research Corporation and the Research Foundation of the State University of New York for financial support of this work.

[4] P. A. D. DE MAINE and R. WIGGIN. In preparation.

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INORGANIC SALTS DISSOLVED IN NON-AQUEOUS OR IN MIXED SOLVENTS—IV

CONDUCTANCE STUDIES OF $SnCl_4 \cdot 5H_2O$ AND $SnCl_2 \cdot 2H_2O$ DISSOLVED TOGETHER IN METHANOL–CARBON TETRACHLORIDE

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Abstract—Conductance measurements are reported for $SnCl_4 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$ dissolved together in methanol or in methanol–carbon tetrachloride at 25°C. Empirical relations between the specific conductance and the total concentration of tin chlorides are given. Evidence of specific interaction between Sn(II) and Sn(IV) species is also discussed.

SPECTROPHOTOMETRIC data for Sn(IV) and Sn(II) dissolved together in pure methanol or in methanol–carbon tetrachloride at 20°C show that small quantities of the two species interact reversibily in solution to form a complex whose concentration is decreased at increased methanol concentrations.[1] BROWNE *et al.*[2] have shown that the enhanced ultra-violet absorption found for $SnCl_4 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$ dissolved together in aqueous solutions of hydrochloric acid, results from the formation of small amounts of a weak complex (ΔH = 600 cal/mole) thus: Sn(IV) + Sn(II) ⇌ complex. The absorption due to the complex in methanol or in methanol-carbon tetrachloride[1] is significantly less than the absorption of the complex in concentrated hydrochloric acid-water solution.[2]

These data suggest that for both aqueous and non-aqueous solvents, at least one of the two interacting mononuclear Sn species may be an ion. In the present work detailed conductometric studies for the mixed tin chlorides dissolved in methanol or in methanol–carbon tetrachloride are reported.

EXPERIMENTAL

Chemicals and techniques are described in the paper III of this series.[3]

Reproducibility tests showed that the measurements were accurate to within one percent if the nitrogen purged materials were handled only in a dry nitrogen atmosphere. With such conditions no change in the resistance values was observed even after one hour.

Concentrations studied were: methanol—three concentrations between 24·56 and 16·70 mole/l. with carbon tetrachloride as diluent; $SnCl_2 \cdot 2H_2O$ plus $SnCl_4 \cdot 5H_2O$—sixteen concentrations between $4{\cdot}94 \times 10^{-3}$ and 0·988 mole/l. for each solvent composition.

RESULTS

The molar conductance for Sn(IV) plus Sn(II) dissolved in methanol or in methanol–carbon tetrachloride is significantly less than the summed molar conductances for the salts dissolved separately in the same solvent (Table 1). Plots of

[1] P. A. D. DE MAINE and M. M. DE MAINE, *J. Inorg. Nucl. Chem.* **11**, 144 (1959).
[2] C. I. BROWNE, R. P. CRAIG and N. DAVIDSON, *J. Amer. Chem. Soc.* 73, 1946 (1951).
[3] P. A. D. DE MAINE, M. M. DE MAINE and G. E. MCALONIE, *J. Inorg. Nucl. Chem.* **14**, 268 (1960).

the molar conductance versus the square root of the combined tin concentrations have the same general characteristics and shapes as the corresponding plots for the separate salt solutions.[3] For the combined salts, the linear portions cover a greater relative salt concentration range; and positive slopes occur for much higher methanol concentrations.

Plots of the specific conductance versus the total salt concentration for constant solvent compositions again yielded two intersecting straight lines with sharp

Table 1.—Calculated (μ_C)* and measured (μ_M) molar conductances for $SnCl_4 \cdot 5H_2O$ plus $SnCl_2 \cdot 2H_2O$ dissolved in solvent mixtures with the indicated methanol concentrations (M)

Salt conc. (mole/l. × 10^5)		M = 24·56 (mole/l.)		M = 20·62 (mole/l.)		M = 16·69 (mole/l.)	
Sn(II)	Sn(IV)	μ_C	μ_M	μ_C	μ_M	μ_C	μ_M
2·60	2·34	—	37·8	71·8	28·5	48·1	16·8
5·20	4·68	81·1	28·2	52·3	17·5	30·9	10·7
15·59	14·05	44·0	14·3	29·0	10·6	16·7	5·90
25·99	23·42	33·6	11·4	22·7	8·29	13·6	5·19
36·36	32·79	31·7	9·93	19·5	7·49	12·2	4·68
51·98	46·84	24·9	8·89	17·1	6·78	11·1	4·54
78·0	70·3	21·4	8·43	15·2	6·68	10·2	—
104·0	93·7	19·4	8·06	14·1	6·53	9·9	4·60
155·9	140·5	17·6	7·99	13·1	6·54	9·34	5·09
207·9	187·4	16·7	—	14·0	6·73	9·28	5·24
259·9	234·2	15·9	8·15	12·4	6·82	9·27	5·46
311·9	281·0	15·7	8·08	12·5	6·86	9·33	5·53
363·9	327·9	15·1	7·82	—	6·86	9·24	5·65
415·8	374·7	15·2	—	11·9	6·84	9·49	6·17
467·8	421·6	14·9	7·92	12·4	6·90	9·51	—
519·8	468·4	14·8	7·73	12·0	6·81	9·45	—

* μ_C is the sum of the molar conductances for separate solutions of the two salts with identical solvent composition. Temperature 25°C.

transition points (Fig. 1). Specific conductance and the slopes of both straight lines are again decreased by increased proportions of carbon tetrachloride. The salt concentrations at the point of intersection were 0·101, 0·106 and 0·162 mole/l. for solutions with 24·56, 20·62 and 16·69 moles/l. of methanol respectively.

DISCUSSION

A detailed theoretical examination of both the spectrophotometric[1] and the conductometric data, for tin chlorides is in progress.[4] The complexity of the mixed and separate salt systems is such that at present only general conclusions can be drawn.

The decrease in molar conductance when both salts are dissolved together in methanol or in methanol–carbon tetrachloride (Table 1) may be due to specific

[4] P. A. D. de Maine and R. Wiggin. In preparation.

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interaction between mononuclear species of Sn(II) and Sn(IV) alone. As the decrease in molar conductance is very much larger than the decrease with increasing salt concentration for the separate solutions (Table 1) the phenomenon cannot be attributed to the common ion effect. Of several possible modes of interaction, that between a Sn(II) ion and a Sn(IV) ion seems most likely.

The low values reported for the molar conductance of the single salt and the two

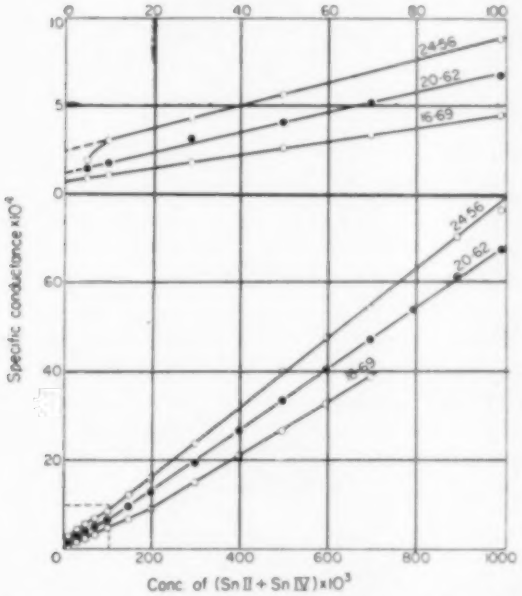

FIG. 1.—Plots of the specific conductance versus the total tin salt concentration for $SnCl_2 \cdot 2H_2O$ plus $SnCl_4 \cdot 5H_2O$ dissolved in mixtures of methanol and carbon tetrachloride with the indicated methanol concentration. All concentrations are in mole/l.

salt solutions (Table 1) suggest that only a small portion of each salt is ionized. Simple calculations show that approximately 40 per cent of the ionized Sn(IV) and Sn(II) species combine in pure methanol.* These calculations also show that less than one per cent of the total Sn(II) and Sn(IV) species combine in this way.

Since the per cent decrease in molar conductances increases at decreased methanol concentrations, (Table 1) the number of ions entering into binary combinations must increase. This suggests that "solvation" by methanol of at least one Sn(II) or Sn(IV) ion species must prevent interaction. These results and conclusions are in complete accord with published spectrophotometric data.

Acknowledgements—Financial support by the Research Corporation and by the Research Foundation, State University of New York is gratefully acknowledged.

* In these calculations we assumed that both salts ionized only once, and the two positively charged tin ions combine thus: Sn(II) ion + Sn(IV) ion ⇌ complex. The limiting molar conductances were assumed to be fifty for the three tin ions and 70 for Cl^-.

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 276 to 282. Pergamon Press Ltd. Printed in Northern Ireland

SEPARATION OF ACIDIC ESTERS OF PHOSPHORIC ACID BY ION EXCLUSION—I

THE SEPARATION OF MONO- AND DIBUTYLPHOSPHATE*

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Abstract—A new technique for the separation of alkyl phosphoric acids, based on ion exchange, is described. A mixture of mono-n-butyl-phosphate (H_2MBP) and di-n-butyl-phosphate (HDBP) was successfully separated on a Dowex 50 resin bed. Up to 5 g of mixture per 100 ml of resin can be separated by eluting with water. The yields are up to 85 per cent and the purity is better than 99 per cent. The data obtained are discussed. The HDBP is rather strongly adsorbed on the resin and some evidence is given of a complex formation between the resin sulphonic group and two molecules of HDBP.

THE organophosphoric acids are often available as mixtures of mainly mono- and di-esters with variable quantities of pyroesters and free alcohol. Various methods for the separation of these mixtures are reported in the literature: fractional crystallization of the barium salts developed by PLIMMER and BUNCH[1]; or, by solvent extraction which gives even better results. However, the most convenient method is that developed by STEWART and CRANDALL[2] which was later improved by PEPPARD *et al.*[3,4]

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As far as it is known, no one has considered the possibility of separating the mixture by ion exclusion on a cation exchange resin. This method appears particularly attractive when one considers that those acids readily form hydrogen bonds. The ion exclusion method is suitable for separating components of different ionic strengths using a cation exchange resin. No chemical regenerants are required other than water. When an ion exchange resin is placed in a dilute solution of an electrolyte, the concentration of that electrolyte is lower in the aqueous portion of the resin phase than in the surrounding solution.

Such behaviour of the distribution of ionic solutes between water and resin led to the name "ion exclusion".[5,6] Generally speaking, it has been found that non-ionic compounds are more retained inside the resin particles whereas ionic solutes are more readily excluded.

MATERIALS AND METHODS

Preparation of the mixture of H_2MBP *and* HDBP. Seventy grammes of P_2O_5 (analytical grade) were put in a round-bottomed flask with four outlets into which were fitted a thermometer, a stirrer, a separatory funnel and a condenser. The flask was then placed in an ice-bath (to keep the temperature

* Mono-n-butyl-phosphate will be abbreviated as H_2MBP and di-n-butyl-phosphate as HDBP.[1]

[1] R. H. A. PLIMMER and W. J. N. BUNCH, *J. Chem. Soc.* 292 (1929).
[2] D. C. STEWART and H. W. CRANDALL, *J. Amer. Chem. Soc.* **73**, 1377 (1951).
[3] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[4] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).
[5] R. M. WHEATON, W. C. BAUMANN, *Industr. Engng. Chem.* **45**, 228 (1953).
[6] W. C. BAUMANN, R. M. WHEATON and D. W. SIMPSON, *Ion Exclusion, Ion Exchange Technology*. Academic Press, New York (1956).

as low as possible) and 140 ml of n-butyl alcohol (analytical grade) were added dropwise and the mixture was stirred vigorously.

After the addition of BuOH, the temperature was raised to 95°C, and the solution was left at this temperature for about 4 hr. The final solution contains H_2MBP, HDBP, small amount of H_3PO_4, n-butyl alcohol and sim.-di-(n-butyl)pyrophosphoric acid. A potentiometric titration method was used for analyses of the components of the mixture,[7] and purification of the components, when necessary, was carried out according to the procedure of STEWART and CRANDALL[8] which was modified and improved by PEPPARD *et al.*[3,4]

TABLE 1

Batch	1	2	3	4	5	6	7
Molarity of H_2MBP	0·018	0·035	0·053	0·071	0·141	0·212	0·282
Molarity of HDBP	0·011	0·022	0·033	0·044	0·089	0·133	0·178
Total molarity	0·029	0·057	0·086	0·115	0·230	0·345	0·460
$K_d(H_2MBP)$	0·30	0·30	0·34	0·36	0·49	0·62	0·72
K_d(HDBP)	0·87	1·00	1·20	1·40	2·24	5·57	9·22
Separation factor $\alpha = \frac{K_d(HDBP)}{K_d(H_2MBP)}$	2·9	3·3	3·5	3·9	4·6	9·0	12·8

Batch experiments. The feasibility of separation of these components by ion exclusion can be determined from the distribution coefficients (K_d) calculated from batch experiments:

$$K_d = \frac{Cr}{C} \tag{1}$$

where Cr is solute concentration in the solution within the resin particles (milliequivalent/gramme of dry resin) and C is the solute concentration in the surrounding solution (milliequivalent/ml of solution).

In order to obtain the K_d values the cation exchange resin Dowex 50, X8, acid form, 50–100 mesh, was employed. The resin was washed with ten times its volume of 1N HCl and after with distilled water until the reaction produced with $AgNO_3$ disappeared. To 50 ml of settled resin, 100 ml of H_2O and a known amount of the mixture of HDBP and H_2MBP was added. The resin was stirred for two hours, and later it was allowed to settle for 14 hr at room temperature. Fifty millilitres of the solution were filtered through a sintered glass filter, and titrated with NaOH by potentiometric titration.

The K_d was expressed for HDBP as follows:

$$K_d(HDBP) = \frac{\text{Total HDBP (mmoles)} - \text{HDBP in solution (mmoles)}}{\text{HDBP in solution (mmoles)}}$$

add for H_2MBP as follows:

$$K_d(H_2MBP) = \frac{\text{Total } H_2MBP \text{ (mmoles)} - H_2MBP \text{ in solution (mmoles)}}{H_2MBP \text{ in solution (mmoles)}}$$

K_d is dependent on the type of resin, the degree of cross-linkage, the concentration of the solute, and the presence of additional solutes in the same solution. If two solutes have different values of the distribution coefficient the separation of the two by ion exclusion can be accomplished. Furthermore, if the K_d value is known, it is possible to predict the appearance of a solute in the effluent, and the degree of separation by the column. The K_d values for H_2MBP and HDBP were measured at different concentrations of a mixture of the two. These values are reported in Table 1. In Fig. 1 the Cr values

[7] S. KENNEDY and S. S. GRIMLEY, AERE CE/R 968 (1953).

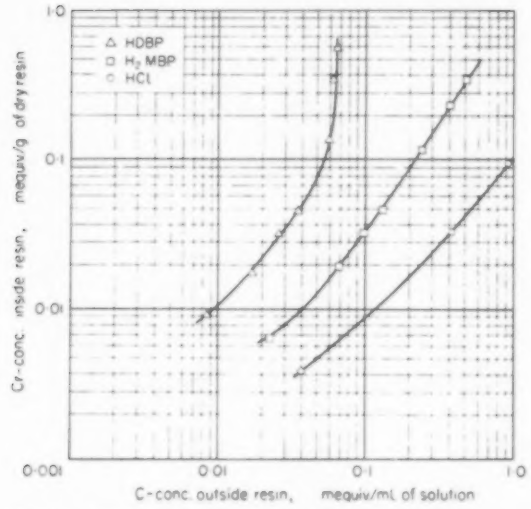

FIG. 1.—Equilibrium distribution of HDBP, H_2MBP and HCl between resin Dowex 50 and aqueous solution.

for H_2MBP and HDBP are plotted versus the correspondent C values of the two acids. A similar curve which shows the behaviour of HCl plotted from the data of BAUMANN and EICHHORN[8] is reported for comparison.

The values of the separation factor (α) expressed as follows:

$$\alpha = \frac{K_d(\text{HDBP})}{K_d(\text{H}_2\text{MBP})} \tag{2}$$

are reported in Table 1.

The variation of the α values versus the concentration of the two acids is shown in Fig. 2. From the curve in Fig. 2 it appears that the α value increases with increasing concentration of the two acids,

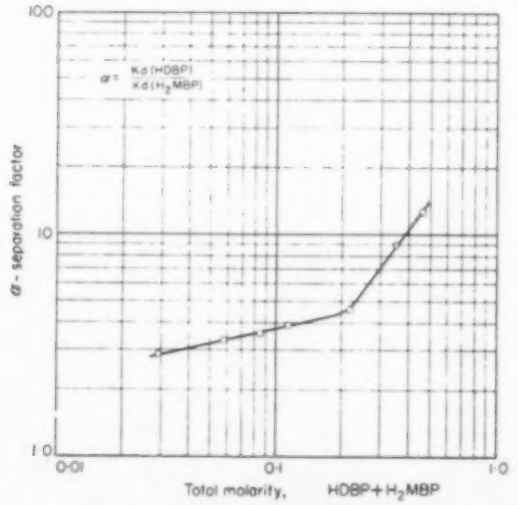

FIG. 2.—Effect of the initial concentration of HDBP and H_2MBP on the separation factor (α).

[8] W. C. BAUMANN and J. EICHHORN, *J. Amer. Chem. Soc.* **69**, 2830 (1947).

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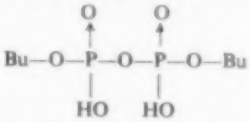
to a maximum value of 12·8. Thus the separation of the mixture appears feasible over a considerable range of concentration.

Column experiments. Separations by the column technique were performed as follows: the column was 1·15 cm diameter and 180 cm high, the resin, Dowex 50, X8, 50–100 mesh, acid form; and the feeding solution was a crude mixture containing: H_2MBP, 3·48 HDBP, 2·46 H_3PO_4, 0·20 mmole/ml and small amounts of sym.-di-(n-butyl)pyrophosphoric acid:



Sym.-di-(n-butyl)pyrophosphoric acid and H_3PO_4 are eluted first, followed by H_2MBP and finally HDBP. Fig. 3 shows a typical elution curve of the separation. Several separations were performed with different quantities of feeding solution, keeping constant all other conditions.

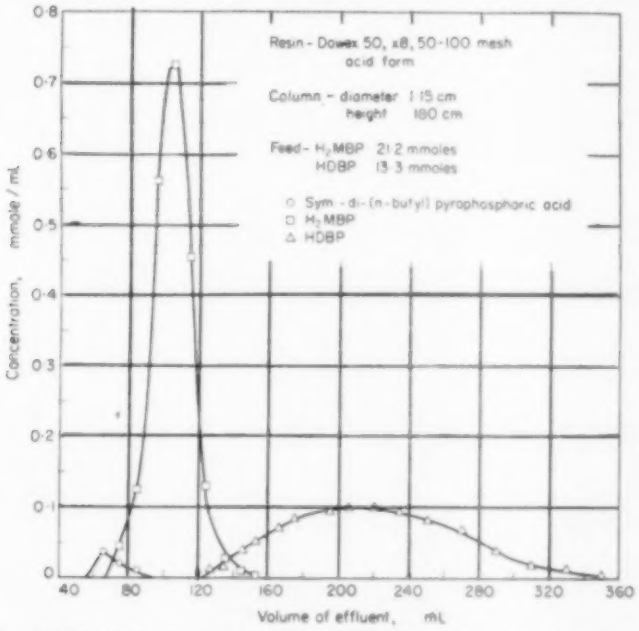


FIG. 3.—Typical elution curve. Separation of sym.-di-(n-butyl) pyrophosphoric acid, H_2MBP and HDBP on a Dowex 50 resin bed.

From the results obtained by column separation we were able to calculate (by means of the equations given by SIMPSON and WHEATON[9]) the number of theoretical plates (P), the height of a theoretical plate ($HETP$), the distribution coefficients (K_d) and the separation factor (α).

$$P = \frac{2\,V_m(V_m - V_{1/2})}{W^2} \tag{3}$$

$$HETP = \frac{H}{P} \tag{4}$$

$$K_d = \frac{V_m - V_{1/2}}{V^2_{1/2}} \tag{5}$$

$$\alpha = \frac{K_d(\text{HDBP})}{K_d(H_2MBP)} \tag{6}$$

[9] D. W. SIMPSON, R. M. WHEATON, *Chem. Engng. Progr.* **50**, 45 (1954).

where: V_m = volume of the effluent of maximum concentration of the solute in millimetres.
W = the half-width of the elution curve of an ordinate of $1/e$ of the maximum number of millilitres, ($e = 2{\cdot}718$)
H = the height of the column in centimetres
V_{ilq} = the interstitial volume in millilitres
V^{r}_{ilq} = the liquid occluded within the resin in millilitres.

The V_{ilq} and V^{r}_{ilq} values were measured following the procedure developed by WHEATON and BAUMANN[3].

For the particular batch of resin which we employed, the following was obtained: $V_{\text{ilq}} = 0{\cdot}30$ ml/ml of wet resin, $V^{r}_{\text{ilq}} = 0{\cdot}42$ ml/ml of wet resin.

The results of the column experiments are summarized in Table 2. As shown in Fig. 4, on the

TABLE 2

Test	1	2	3	4	5	6
Feeding						
H_2MBP (mmole)	1·74	3·48	5·22	7·50	11·25	22·20
HDBP (mmole)	1·23	2·46	3·33	4·75	7·12	13·32
Total	2·97	5·94	8·55	12·25	18·37	35·52
Elution						
V_{max} H_2MBP(ml)	110	115	113	115	110	105
V_{max} HDBP(ml)	150	185	168	194	196	222
Flux (ml/min per cm²)	0·17	0·17	0·17	0·17	0·17	0·17
*HETP** of H_2MBP(cm)	13·1	7·7	1·4	1·8	2·1	4·3
*HETP** of HDEP(cm)	3·0	2·1	4·5	3·7	7·1	15·5
K_d calculated for H_2MBP	0·74	0·80	0·78	0·80	0·74	0·67
K_d calculated for HDBP	1·26	1·72	1·50	1·84	1·87	2·21
Separation factor						
$\alpha = \frac{K_d(\text{HDBP})}{K_d(\text{H}_2\text{MBP})}$	1·70	2·15	1·92	2·30	2·52	3·30

* *HETP* = height equivalent of a theoretical plate.

column the α values for the column experiments increase with increasing amount of feeding solution. This is in good agreement with the batch tests reported above.

RESULTS AND DISCUSSION

From our data, it appears that the method of ion exclusion is suitable for separating a mixture of H_2MBP and HDBP. The advantages of this method are:

(1) The column can be fairly heavily loaded: e.g. up to 5 g of mixture per 100 ml of resin can be separated, ca. 85–90 per cent of H_2MBP and HDBP are recovered with a purity greater than 99 per cent.
(2) The crude mixture can be used without any preliminary purification.
(3) The resin does not require any regeneration at the end of each separation. The column is ready for a new cycle as soon as the HDBP is eluted.

Preliminary tests indicate that the method can be used to separate different types of organoesters of phosphoric acid. The results of this research will be published at a later date. The actual mechanism of the separation does not depend solely upon

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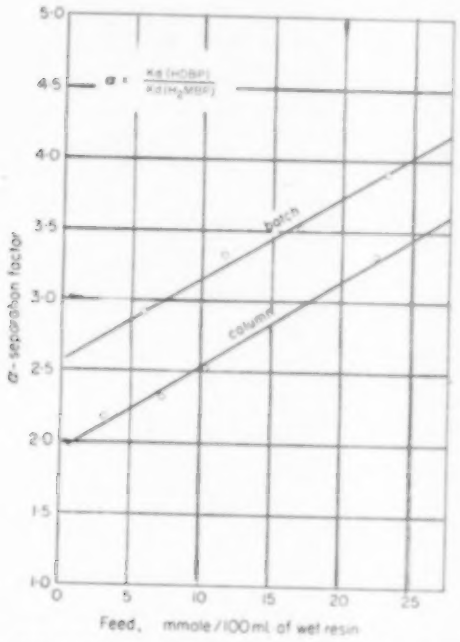


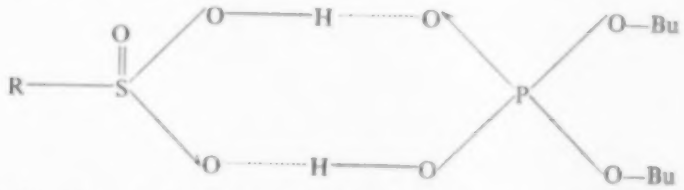
FIG. 4.—Variation of the separation factor in column and in batch with feeding.

selective exclusion of the anion from the resin particles. Both acids have relatively high values of the dissociation contants. The following values are given in literature:[10]

$$pk_1\ (H_2MBP) = 1{\cdot}72$$

$$pk\ (HDBP) = 1{\cdot}89$$

Thus they can both be considered strong acids, at least in dilute solutions, and hence the separation cannot fully be explained in terms of different ionic strengths. A better explanation might be that these compounds form weak complexes with the resin sulphonic group, i.e.



Such behaviour is suggested by the work of PEPPARD *et al.*[4] For instance, they found that organo-phosphoric acids are depolymerized by acetic acid because stronger hydrogen bonds are formed. The formation of a weak complex between the resin and the HDBP is supported by the fact that the K_d value for HDBP (Fig. 5) is above unity (from ca. 1 to 9·22), suggesting a rather strong affinity of the resin for this compound. However the K_d value for H_2MBP is always below unity showing

[10] D. W. KUMLER and J. J. EILER, *J. Amer. Chem. Soc.* **65**, 2355 (1943).

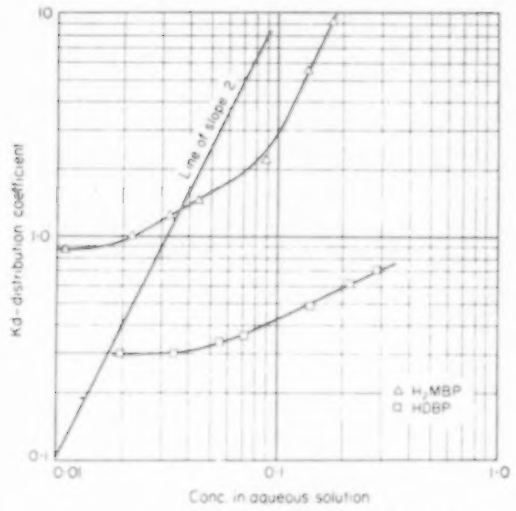
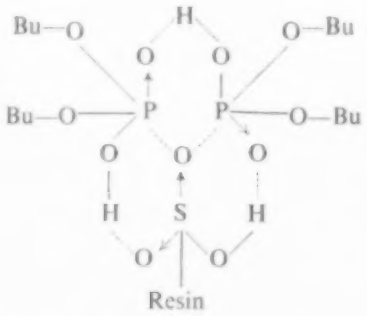


FIG. 5.—Solution concentration dependency of K_d.

a less affinity of the resin for H_2MBP. The structure of the complex (HDBP–Resin) was not investigated. However, it is evident from Fig. 5 that the K_d depends upon the second power of concentration when the molar concentration of HDBP is greater than 10^{-1}. Such behaviour can be interpreted thus: the HDBP forms a complex with the sulphonic group of the resin, viz,

$$\text{Resin—}SO_3H \ldots (HDBP)_2$$

If we consider the tendency of HDBP to dimerize[4] the structure of the complex might be:



On dilution, water breaks this complex, acting as a depolymerizing solvent.

Acknowledgements—In its earlier stage this work was performed in the Chemistry Laboratory of C.I.S.E., Milano. The supervision of Dr. CERRAI is gratefully acknowledged. We would like to thank Dr. BERTOLINI whose kind hospitality permitted the work to be accomplished in the Radiochemistry Laboratory of C.N.R.N.–Ispra.

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J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 283 to 287. Pergamon Press Ltd. Printed in Northern Ireland

THE DENSITY OF LIQUID ALUMINIUM OXIDE*

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(*Received* 24 *August* 1959; *in revised form* 10 *October* 1959)

Abstract—Using a molybdenum crucible and a tungsten sinker, the density of liquid aluminium oxide was determined by the loss in weight of an immersed sinker method over a temperature range of 2375–2625°K. The liquid molar volumes were calculated for various temperatures and the expansion of the oxide on melting was determined.

A BASIC knowledge of the physical properties of materials at high temperatures is becoming of increasing importance. A check of the literature on the density and surface tension of molten oxides and salts showed that very little data are available above 1700°K. The only data available were determined by means of the drop method[1,2,3,4] at the melting points of the oxides and salts. The lack of data at temperatures above the melting point is due mainly to the absence of suitable material that could withstand these high temperatures.

At elevated temperatures it is difficult to find materials which will not react with the melts and at the same time endure these temperatures. Platinum and iridium, which are normally used, were not suitable because their melting and softening points are too low. After some study, the authors[5] found that a tungsten sinker and graphite crucible could be used with molten fluorides at these elevated temperatures.

When working with molten aluminium oxide, the tungsten float could still be used, but the graphite crucible could not because

$$Al_2O_3 + 3C \longrightarrow 2Al + 3CO.$$

Due to its high cost of fabrication tungsten was not used as the crucible. Further studies showed, however, that molybdenum was suitable and crucibles were readily available.

Using the tungsten sinker and molybdenum crucible, the density of liquid aluminium oxide was determined by the loss in weight of an immersed sinker method over a temperature range of 2375–2625°K.

EXPERIMENTAL

Apparatus

In these studies, the source of heat was a carbon tube resistance furnace in an argon atmosphere. It consisted of (*C*) a 3 in. carbon tube (grade GA National Carbon pipe, 97 per cent carbon) with

* This research was sponsored by the National Science Foundation.

[1] H. V. WARTENBERG, G. WEHNER and E. SARAN, *Nachr. Ges. Wiss. Gottingen, Jahresber. Gesschaftsjahr, Math.—physik. Klasse. Fachgruppen II (N.F.)* **2**, 73 (1936).
[2] A. W. PETERSON, H. KEDESDY, P. H. KECK and E. SCHWARZ, *J. Appl. Phys.* **29**, 213 (1958).
[3] A. CALVERLEY, *Proc. Phys. Soc.* B **70**, 1040 (1957).
[4] W. D. KINGERY, *J. Amer. Ceramic Soc.* **42**, 6 (1959).
[5] A. D. KIRSHENBAUM, J. A. CAHILL and C. S. STOKES, *The Density of Metal Oxides and Fluorides from* 1500° *to* 2500°K. Paper presented before the High Temperature Session of the Division of Industrial & Engineering Chemistry, at the Boston meeting of the American Chemical Society, April 12, 1959.

(*E*) copper electrodes on each end. The tube was centered in a metal shell and insulated with (*F*) Thermax carbon black. The furnace lids (*D* and *L*) were made of transite. Argon (*A*) was fed into the furnace through the metal shell and at the bottom through the transite lid (*L*).

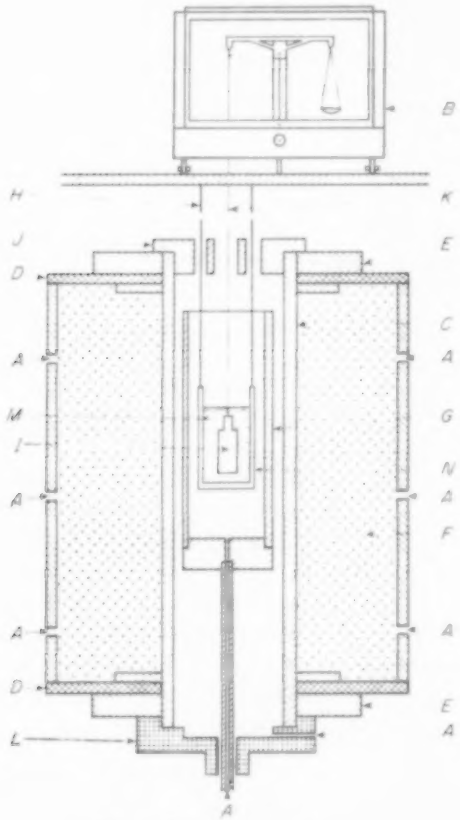

FIG. 1—Density apparatus.

A—Argon
B—Analytical balance
C—Carbon tube
D—Transite lids
E—Copper electrodes
F—Thermax
G—Graphite chimney
H—Molybdenum wires
I—Tungsten sinker
J—Graphite lid
K—Tungsten wire
L—Transite lid
M—Aluminium oxide melt
N—Molybdenum crucible

When determining the density of molten aluminium oxide, a molybdenum crucible (*N*) 2$\frac{3}{4}$ in. high and 1$\frac{1}{2}$ in. diameter was used. It was suspended by molybdenum wires (*H*) in the center of the furnace surrounded by a graphite chimney (*G*) as shown in Fig. 1. A stream of dried argon (*A*) entered the bottom of the chimney and engulfed the crucible. The tungsten sinker (I), $\frac{1}{4}$ in. diameter and 1 in. high, was suspended from an analytical balance (*B*) through a graphite lid (*J*) into the oxide melt (*M*) by means of a tungsten wire (*K*).

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Procedure

The procedure used in these measurements consisted of weighing the sinker in the molten oxide while determining simultaneously the furnace temperature by means of a calibrated optical pyrometer The pyrometer was calibrated by measuring the melting points of nickel, platinum and iridium under black-body conditions. The reproducibility of the pyrometer readings was ±15°K. By taking many readings, however, the final temperature values had a probable error of 2°K or 0·08 per cent. The readings were made on the graphite chimney at the level of melt and were corrected for the emissivity of the graphite.

At these elevated temperatures it was necessary to protect the crucible and sinker from water and air since they would react to form oxides of molybdenum and tungsten. This was achieved by working in an argon atmosphere which was predried and passed over hot magnesium.

The volume of the tungsten sinker was always corrected to the operating temperature by the following equation, making use of the linear coefficient of expansion (α):

$$V_{T_2} = V_{T_1}[1 + 3\alpha(T_2 - T_1)].$$

The α's used in these corrections were those reported by WORTHING[6] and are summarized as follows:

Temperature (°K)	$\alpha \times 10^6$
2000	6·49
2200	7·01
2400	7·54

The density of the tungsten used was 19·222 g/cm³ at 298·5 K (25·3 C).

The density of the melt was calculated from the equation

$$D = \frac{W_A - W_M}{V_{T_2}}$$

where W_A and W_M are the weights of the sinker in air and melt, respectively, and V_{T_2} is the volume of the sinker at the temperature of the melt. The value obtained was corrected for the buoyancy of air (vacuum correction) by making use of the equation:

$$D_w\left[\frac{W_1 + l}{W_a + l}\right] = D_m$$

where D_w = density of the tungsten
D_m = density of the melt
W_1 = apparent loss of weight by the substance
W_a = weight of the sinker in air
and l = weight of air displaced by the sinker or by an equal volume of melt.

Materials used

The aluminium oxide used in these studies was fused aluminia obtained from Morganite Incorporated and had a purity of 99·96% Al_2O_3.

At these high temperatures, it was necessary to be sure that the molten oxide did not react with the crucible. If Al_2O_3 reacted with the crucible, MoO_3 and Al would form

$$Al_2O_3(l) + Mo(s) \longrightarrow MoO_3(g) + 2\,Al(g).$$

as well as AlO and the intermediate coloured oxides of molybdenum. The AlO on cooling, however, forms Al_2O_3 and Al

$$3AlO \longrightarrow Al_2O_3 + Al$$

Some Al_2O_3 was melted in a molybdenum crucible and then analysed for Al and MoO_3. The melt which was still colourless contained neither aluminium nor any oxide of molybdenum.

[6] A. G. WORTHING, *Phys. Rev.* **10**, 638 (1917).

RESULTS

The only data available on the density of liquid Al_2O_3 were those reported by WARTENBERG[1] and KINGERY[1]. They reported values of $2{\cdot}5 \pm 0{\cdot}1$ and $2{\cdot}97 \pm 0{\cdot}05$ g/cm³, respectively, at a few degrees above the melting point of Al_2O_3 (2320 ± 15°K).

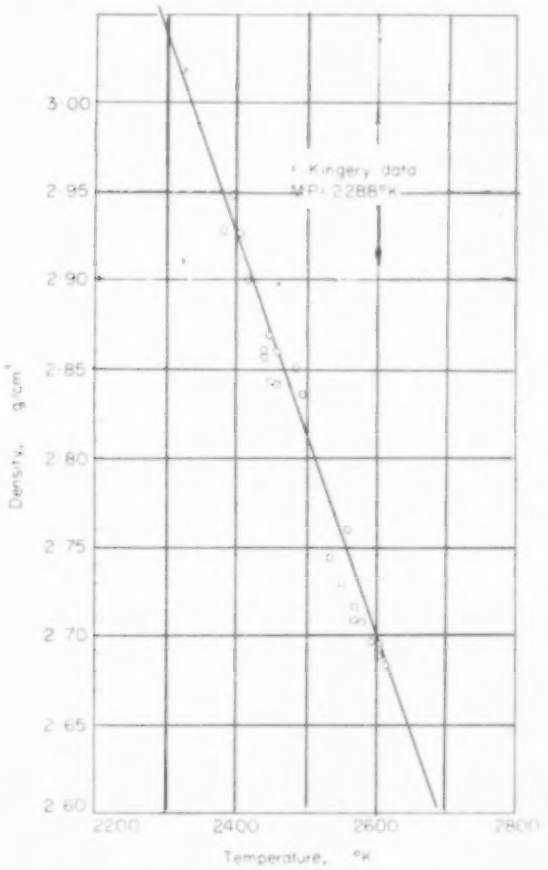

FIG. 2.—Density of liquid Al_2O_3.

Using the method described above, the density of liquid Al_2O_3 was determined from 2375 to 2625°K. The values obtained are tabulated in Table 1 and fall on a straight line as shown in Fig. 2 when density is plotted against temperature. The equation of this straight line is

$$D = 5{\cdot}632 - 1{\cdot}127 \times 10^{-3}T.$$

The smoothed values and the corresponding molar volumes obtained from this equation are given in Table 2.

The density of liquid Al_2O_3 at its melting point gives a liquid density of 3·053 g/cm³ and a molar volume of 33·40 cm³/mole. Extrapolation of expansion data for

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TABLE 1.—DENSITY OF LIQUID Al_2O_3

Temperature (°K)	Density (g/cm³)	Temperature (°K)	Density (g/cm³)
2383	2·929	2497	2·836
2396	2·948	2535	2·745
2405	2·926	2549	2·730
2418	2·900	2560	2·761
2442	2·861	2569	2·717
2442	2·857	2569	2·710
2447	2·869	2580	2·708
2452	2·844	2594	2·698
2461	2·860	2606	2·695
2461	2·843	2606	2·693
2487	2·852	2606	2·690
		2616	2·685

TABLE 2.—MOLAR VOLUMES OF MOLTEN Al_2O_3

Temperature, (°K)	Density (g/cm³) (smoothed values)	Molar volume (cm³/mol)
2300	3·040	33·54
2400	2·927	34·83
2500	2·814	36·23
2600	2·702	37·74
(m.p.) 2288	3·053	33·40

the solid[7] to its melting point gives a solid density of 3·73 g/cm³ or a molar volume 27·3 cm³/mole. Thus aluminium oxide expands 22 per cent upon melting assuming Ebert's solid data is correct.

Acknowledgement—The authors wish to thank Dr. A. V. GROSSE for his helpful suggestions.

[7] H. EBERT and C. TINGWALDT, *Z. Physik.* **37**, 471 (1936).

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 288 to 305. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

A preparation of carrier-free iodate*

(*Received* 1 *March* 1960)

CARRIER-FREE iodate has been prepared employing cerium (IV),[1] chromium (VI),[2] and manganese (VII)[3] as oxidizing agents. We wish to report a study of the oxidation of carrier-free iodine to iodate by nitric acid which has led to a procedure for the preparation of solutions of carrier-free iodate free of metal cations.

Iodine-131 obtained from Oak Ridge was purified according to the procedure of KAHN *et al.*[4] Analytical Reagent Grade nitric acid was treated with nitrogen to remove dissolved oxides of nitrogen. Nitric acid solutions of carrier-free iodine-131 were sealed in Pyrex tubes and heated in the absence of light in a constant-temperature oven. The reaction mixtures were subsequently analysed for iodate as described elsewhere.[1]

The results of the oxidation of iodine-131 by nitric acid, which are summarized in Figs. 1–3, indicate that carrier-free iodate can be prepared in essentially quantitative yields by oxidation in

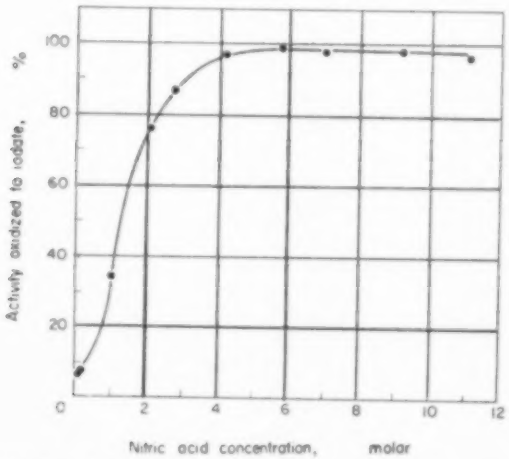

FIG. 1.—Oxidation of carrier-free iodine to iodate in nitric acid solutions at 150°C for 3 hr.

5·76 M nitric acid at 150°C for 3 hr. Oxidation at higher concentrations (> 8 M) of nitric acid is undesirable because of the formation of oxides of nitrogen which tend to reduce the iodate.

Evaporation of 5·76 M nitric acid solutions of carrier-free iodate to dryness in the dark, under 0·1 mm Hg, at room temperature, with subsequent dissolution of the residue in distilled water, resulted in recovery of 88–98 per cent of the activity, all in the form of iodate. Evaporation under similar conditions in the presence of ordinary laboratory lighting resulted in recovery of only about 3 per cent of the activity. Low yields were also obtained on evaporation under a heat lamp or over a steam bath in the presence of light. Presumably, the oxides of nitrogen formed in the presence of light reduce the iodate to iodine which is then volatilized.

* This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission (Contract No. AT(11-1)-733).

[1] M. KAHN and A. C. WAHL, *J. Chem. Phys.* **21**, 1185 (1953).
[2] H. M. EILAND, Doctoral Dissertation, University of New Mexico (1957).
[3] A. P. MUSAKIN and L. V. PUCHKOV, *Zh. Neorg. Khim.* **4**, 483 (1959).
[4] M. KAHN, A. J. FREEDMAN and C. G. SHULTZ, *Nucleonics* **12**, No. 7, 72 (1954).

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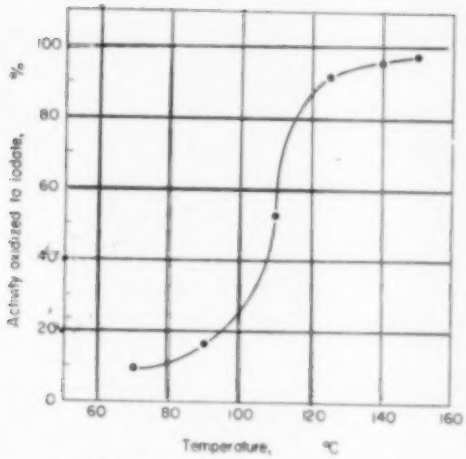

FIG. 2.—Oxidation of carrier-free iodine to iodate at various temperatures in 5·76 M nitric acid for 3 hr.

Studies of the formation of iodate in 5·76 M nitric acid solutions of carrier iodide which were heated for 3 hr at 150°C revealed a dependence on the total iodide concentration. For minimum iodide concentrations ranging from 10^{-4} to 10^{-6} M, about 85 per cent of the iodide was oxidized to iodate; at 10^{-7} M, 93 per cent of the iodide was oxidized to iodate.

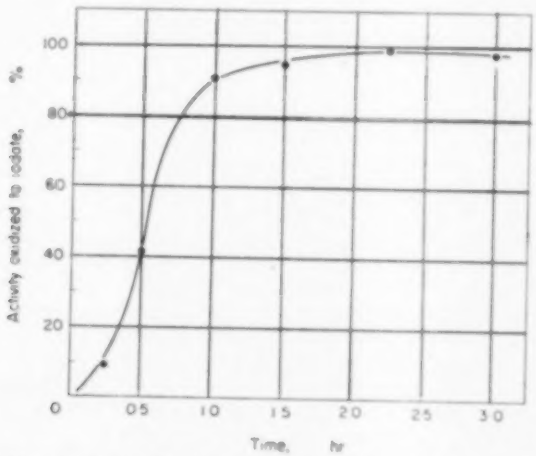

FIG. 3.—Oxidation of carrier-free iodine to iodate at 150°C in 5·76 M nitric acid as a function of time.

There was no detectable decomposition of carrier-free iodate in nitric acid solutions (1–14 M) stored at room temperature under ordinary laboratory lighting conditions for at least one week.*

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* The rate of decomposition of nitric acid by light at room temperature is a strong function of the nitric acid concentration. Thus, on evaporation of nitric acid solutions to dryness at room temperature in the presence of light wherein the concentration of nitric acid may reach as high as 16 M, brown fumes were easily detected, whereas solutions of nitric acid of concentration no higher than 14 M did not show discoloration after one week of exposure to the same lighting conditions.

Formation of triethanolamine borate in aqueous solution

(*Received* 4 *March* 1960)

BROWN and FLETCHER[1] showed that when solid triethanolamine borate is dissolved in water, it is slowly transformed into a basic substance which can be titrated with strong acid. These investigators indicated that in the solid state triethanolamine borate had a "triptych" structure. It seems entirely possible that the "triptych" form of the triethanolamine borate chelate was being transformed into the "cage" structure which could be titrated. The idea that the chelate might exist in water suggested that it might form in water. In their study BROWN and FLETCHER showed that addition of acid to a freshly prepared solution of the solid triethanolamine borate in water containing methyl red indicator results in an immediate change of the indicator to its acid colour, followed by slow neutralization and return of the indicator to its basic colour. This characteristic behaviour was exhibited by aqueous solutions prepared with triethanolamine and boric acid, thus demonstrating that triethanolamine borate was formed in water.

To determine the approximate amount of the chelate formed, aqueous solutions of triethanolamine and aqueous solutions of boric acid were mixed and rapidly titrated to the methyl red end point. The titration gives a measure of the basic nitrogen present. By subtracting the amount of titrant consumed from the amount required for complete neutralization, a measure of the amount of nitrogen co-ordinated with the boron is obtained. Three solutions each 0·05 M in triethanolamine and 0·05 M in boric acid were titrated with hydrochloric acid. Complete neutralization required 10·30 m of standard acid. The first solution was titrated immediately after mixing the reactants, and 9·95 ml (97 per cent of total) of titrant were required to reach the first end point. The second solution was titrated after standing at room temperature for 2 hr; it required 8·40 ml (82 per cent of the total). The third solution was placed in an ice-bath for 1 hr after having stood at room temperature for 1 hr; it required 8·30 ml of titrant (81 per cent of the total). These results demonstrate that triethanolamine and boric acid form a chelate in aqueous media and that 18–19 per cent of the triethanolamine is in the triptych form of the chelate. These data do not exclude the possibility that some or all of the basic nitrogen may exist in solution in the cage form.

An estimate of the equilibrium concentration of the triptych form of the chelate was determined by potentiometric titrations. Titrations of triethanolamine borate with hydrochloric acid showed that the equivalence point occurred at a pH of 4·50. Consequently, the rapid titration of aqueous solutions of the chelate to this pH should give the amount of free base present. By subtracting the amount of titrant required for this titration from the amount required for the complete neutralization of the triethanolamine borate, a measure of the concentration of the triptych form of the chelate is obtained. A solution of the chelate which stood at room temperature for six days and which required 19·58 ml of standard acid for complete neutralization was rapidly titrated. To reach a pH of 4·50, 15·86 ml of acid were required; a duplicate determination gave the same result. This shows that 81 per cent of the nitrogen in solution was in an available form, and hence, that 19 per cent of the nitrogen must be co-ordinated with the boron in the triptych structure.

An estimate of the equilibrium concentration of the triptych form of the chelate in butanol solution which stood at room temperature for three days was obtained in the same way. This showed that 22 per cent of the nitrogen present was co-ordinated with boron.

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[1] H. C. BROWN and E. A. FLETCHER, *J. Amer. Chem. Soc.* **73**, 2808 (1951).

The chelation of the ferricinium ion by certain carboxylic acids

(*Received* 7 *March* 1960)

THE addition of ethylenediaminetetra-acetic acid to a solution of the ferricinium ion containing 40 per cent by weight of ethanol gives rise to a colour change from the blue of the ferricinium ion to

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the yellow of a stable chelate. The addition of acid to the solution of the chelate regenerates the ferricinium ion at the same optical density as that previous to chelate formation. In a similar medium the addition of 1:2-diaminocyclohexanetetra-acetic acid, citric acid, oxalic acid and tartaric acid gives rise to yellow chelates in solution.

The ferricinium ion in this medium gives rise to a polarographic wave at +0·16 V[1] whilst on addition of EDTA and adjustment of pH to 3·5 a wave is obtained at −0·14 V with a similar diffusion current to that of the ferricinium ion. The addition of 1:2 diaminocyclohexanetetra-acetic acid at pH 3·5 leads to a wave at −0·13 V. No well-defined waves were obtained with the other reagents at various pH's, although there was a considerable modification of the ferricinium response at +0·16 V.

A Job plot for each reagent showed that a 1:1 chelate was formed in each case, and a spectrophotometric study of ferricinium ion—EDTA solutions at pH 1·90 indicated partial dissociation of the chelate. By the technique described previously,[2] and from measurements of the extinction coefficients of the chelate and of free ferricinium ion log K_s for the ferricinium chelate of EDTA was found to be 17·4. The values of the acid dissociation constants of EDTA used in this determination were those obtained by SCHWARZENBACH[3]. Similar quantitative measurements of optical densities with the other reagents indicated that the strength of chelation is in the decreasing order 1:2 diaminocyclohexanetetra-acetic acid > EDTA > citric acid > oxalic acid > tartaric acid.

In each case, upon increasing the pH the yellow colour of the solution remained substantially the same until pH 7·5, when the solutions assumed a brown coloration which was complete at pH 8·5. Addition of acid to these solutions indicated that the ferricinium ion could be regenerated. On standing, a brown precipitate was formed which consisted substantially of ferric hydroxide.

Experimental

Stock solutions of ferricinium perchlorate in 95% ethanol were obtained by oxidation of ferrocene in 95% ethanol containing perchloric acid at a platinum anode.[1] Reagents were of A.R. grade where possible. The amino carboxylic acids were purified as described previously.[2] Spectrophotometric and polarographic data were obtained as previously indicated, the strength of the solutions being adjusted to 0·1 M by addition of ammonium chloride.

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[1] J. A. PAGE and G. WILKINSON, *J. Amer. Chem. Soc.* **74**, 6149 (1952).
[2] J. K. FOREMAN and T. D. SMITH, *J. Chem. Soc.* 1758 (1957).
[3] G. SCHWARZENBACH, R. GUT and G. ANDEREGG, *Helv. Chim. Acta* **37**, 937 (1954).

A new synthesis of tetramethylethylenediphosphine

(*Received* 9 *March* 1960)

P,P,P′,P′-Tetraalkylethylenediphosphines, a group of powerful chelating agents,[1] have been prepared by stepwise alkylation of phosphine and by addition of tetraalkylbiphosphines to ethylene.[2] A more convenient synthesis has now been found and involves addition of tetramethylbiphosphine disulphide(I), obtainable in 85 per cent yield from methylmagnesium bromide and thiophosphoryl chloride,[3] to ethylene to give P,P,P′,P′-tetramethylethylenediphosphine disulphide(II).

$$\underset{\text{I}}{(CH_3)_2P(S)-P(S)(CH_3)_2} + CH_2{=}CH_2 \rightarrow \underset{\text{II}}{(CH_3)_2P(S)CH_2CH_2P(S)(CH_3)_2}$$

$$\text{II} + 2(C_4H_9)_3P \rightarrow \underset{\text{III}}{(CH_3)_2PCH_2CH_2P(CH_3)_2} + 2(C_4H_9)_3PS$$

[1] C. E. WYMORE, Ph.D. Thesis, University of Illinois (1957).
[2] A. B. BURG, Wright Air Force Development Center Conference on High Temperature Polymers and Fluid Research, May, 1959.
[3] H. REINHARDT, D. BIANCHI and D. MÖLLE, *Ber.* **90**, 1657 (1957).

Desulphurization of II with tributylphosphine gave P,P,P′,P′-tetramethylethylenediphosphine(III) in 78 per cent yield. Although the overall yield is similar to that reported by BURG,[5] this reaction sequence is more suitable for large-scale preparations because it involves no spontaneously flammable materials.

It was also found that tetramethylbiphosphine disulphide(I) itself can be desulphurized with tributylphosphine to give tetramethylbiphosphine(IV) in 69 per cent yield. Triethyl phosphite also serves as a desulphurizing agent in this reaction but gives a lower yield of IV.

$$(CH_3)_2P(S)-P(S)(CH_3)_2 + 2(C_4H_9)_3P \rightarrow (CH_3)_2PP(CH_3)_2 + 2(C_4H_9)_3PS$$

I IV

Experimental

P,P,P′,P′-Tetramethylethylenediphosphine disulphide. Each of four 165 ml Carius tubes was charged with 11·2 g of tetramethylbiphosphine disulphide, 0·3 g of iodide and 2·0 g of ethylene. The tubes were heated at 275° for 48 hr. The light yellow, crystalline product was recrystallized from ethanol to give fine, off-white needles, m.p. 257–263°; yield, 30·5 g (60%). Two more recrystallizations gave pure white P,P,P′,P′-tetramethylethylenediphosphine disulphide, m.p. 260–263°. (Found: C, 33·53; H, 7·55; P, 29·07; S, 30·30. Calc. for $C_6H_{16}P_2S_2$: C, 33·63; H, 7·53; P, 28·92; S, 29·93.)

P,P,P′,P′-Tetramethylethylenediphosphine. A mixture of 19 g of P,P,P′,P′-tetramethylethylenediphosphine disulphide and 40 g of tri-n-butylphosphine[4] was heated to 245° in a nitrogen atmosphere in a 100 ml flask fitted to a 12 in. spinning-band column. The mixture soon became homogeneous and 20 ml of a clear, colourless liquid distilled at 160–190° over a period of 1 hr. Redistillation gave 10·4 g (78%) of P,P,P′,P′-tetramethylethylenediphosphine, b.p. 104°/60 mm; n_D^{25} 1·4887, m.p. −5 to −1° (Lit. values:[2] b.p. 188°, m.p. 0°). The proton magnetic resonance spectrum was identical to that of an authentic sample prepared by addition of tetramethylbiphosphine to ethylene.[2]

A 1·0 g sample of the diphosphine was dissolved in 50 ml of ether and stirred in a nitrogen atmosphere while methyl bromide was bubbled through the solution for 30 min. A white precipitate formed and was collected by filtration. Recrystallization from ethanol gave colourless crystals of P,P,P,P′,P′,P′-hexamethylethylenediphosphonium bromide, m.p. 355–365° with decomposition (Found: C, 28·48; H, 6·58; Br, 47·13. Calc. for $C_8H_{22}Br_2P_2$: C, 28·25; H, 6·52; Br, 47·00.)

Tetramethylbiphosphine. A mixture of 37 g of tetramethylbiphosphine disulphide and 120 ml of tributylphosphine[4] was heated in a nitrogen atmosphere in a flask attached to a 24 in. spinning-band column. When the pot temperature reached 130°, the solid dissolved. A vigorous reaction occurred and 26 ml of cloudy liquid distilled over a period of 15 min. Redistillation gave 16·8 g (69%) of clear, colourless tetramethylbiphosphine, b.p. 139–141°, m.p. −5 to −1° (Lit. vlaues:[5] b.p. 140°, m.p. −2·1°). The proton magnetic resonance spectrum contained a 1–2–1 triplet like that reported by BURG *et al.*[6] The infra-red spectrum contained strong bands assignable to methyl CH and CP bonds and was identical with that of an authentic sample of tetramethylbiphosphine.[7]

When tetramethylbiphosphine disulphide was heated with triethyl phosphite, crude tetramethylbiphosphine, b.p. 139–143°, distilled in 45 per cent yield. However, the infra-red spectrum indicated that the product was contaminated with triethyl phosphite (b.p. 155°).

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[4] The tributylphosphine used in these experiments was supplied by Metal and Thermit Corporation.
[5] A. B. BURG, *J. Inorg. Nucl. Chem.* **11**, 258 (1959).
[6] A. B. BURG, P. J. SLOTA and W. MAHLER, Abstracts of Papers presented at the 134th Meeting of the American Chemical Society, September, 1958, p. 78P.
[7] The author is indebted to Dr. WALTER MAHLER for this comparison of the infra-red spectra.

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Some new hexachloroceric complexes

(*Received* 14 *March* 1960)

ALTHOUGH several attempts have been made[1–4] to isolate hexachloroceric acid crystals in a pure form, success has been achieved only recently.[5] MOOSATH[6] has studied the formation, composition and stability of the ceric pyridinium chloride complex prepared from pure hexachloroceric acid crystals. The isolation and analyses of three new hexachloroceric complexes are reported in this communication.

Hexachloroceric acid crystals (2·5 g) prepared by the method of MOOSATH and RAO[5] were dissolved in 50 ml absolute alcohol. In another vessel, dry piperidine (5 g) in 50 ml alcohol was converted to the hydrochloride. The hydrochloride solution was added dropwise from a separating funnel having a drierite guard tube, which was fitted to the vessel containing the acid solution. Addition of the hydrochloride solution was continued till no more precipitate was formed. The orange-yellow precipitate was separated by filtration under dry conditions. Dry ether was added to the filtrate, when more of the complex was precipitated. The complex was recrystallized from alcohol and was obtained as orange-yellow, needle-shaped crystals. The crystals were washed with ether and kept in a current of dry air for 15 min and analysed for cerium, active-chlorine and total chloride. The complexes with β-picoline and isoquinoline were prepared in the same manner and analysed. The preparation of the complexes was also carried out in dioxane and in methyl alcohol. There was no difference in composition of the products so prepared. The analytical results are presented in Table 1.

TABLE 1.—ANALYSIS OF THE HEXACHLOROCERIC COMPLEXES

Complex	Calculated values (%)			Experimental values (%)		
	Cerium	Active chlorine	Total chloride	Cerium	Active chlorine	Total chloride
Piperidine complex $(C_5H_{11}NH)_2CeCl_6$	26·66	6·76	40·56	26·21	6·34	37·89
β-Picoline complex $(C_6H_7NH)_2CeCl_6$	25·87	6·56	39·36	25·27	5·95	36·92
Isoquinoline complex $(C_9H_7NH)_2CeCl_6$	22·83	5·78	34·73	21·95	5·21	32·95

The low experimental values for total chloride are due to reduction of ceric to cerous with liberation of chlorine, when the complexes are put in water. However, the observed values are above the gram-atom ratio 1 : 5 of cerium to chloride (calc. 1 : 6) and are acceptable, in view of the good agreement between the experimental and calculated values for active-chlorine. Results of further studies on the stability of these complexes will be reported elsewhere.

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[1] J. KOPPEL, *Z. Anorg. Chem.* **18**, 305 (1898).
[2] F. DI STEFANO, *Ann. Chim. Appl.* **12**, 130 (1919).
[3] V. CAGLIOTI, *Atti. Accad. Lincie* **3**, 332 (1926).
[4] A. J. GRANT and C. JAMES, *J. Amer. Chem. Soc.* **37**, 2652 (1915).
[5] S. S. MOOSATH and M. R. A. RAO, *Proc. Ind. Acad. Sci.* **43**, 213 (1956).
[6] S. S. MOOSATH, *Proc. Ind. Acad. Sci.* **49**, 324 (1958).

The reaction of hexamminecobalt(III) chloride with sodium cyanide

(*Received* 16 *March* 1960)

THERE is no record of the synthesis of $[Co(NH_3)_3(CN)_3]$ in the literature. In the course of a programme directed toward the preparation of inorganic polymers this compound became desirable. A possible route to this compound is through the reaction of $[Co(NH_3)_6]Cl_3$ with exactly 3 moles of cyanide ion. The displacement of the chloride from $[Co(NH_3)_6]Cl_3$ should proceed more readily than substitution for the NH_3 because of the closed electronic configuration of the cobalt in $[Co(NH_3)_6]Cl_3$.[1] Thus, it should be possible to replace the chloride ions with cyanide ions in solution and then gradually substitute cyanide for the co-ordinated ammonia. Any $[Co(NH_3)_3(CN)_3]$ formed would be expected to be relatively insoluble in water as it is a "neutral" co-ordination species.

When $[Co(NH_3)_6]Cl_3$ and NaCN were combined in 1 : 3 ratio in water, there was only slight precipitation at 5°C, whereas at room temperature somewhat more precipitate slowly formed. At 80°C the best yield of product was obtained, and precipitation was substantial after a few minutes. The precipitate, however, proved by X-ray to be identical with authentic $[Co(NH_3)_6][Co(CN)_6]$ prepared by the reaction of $[Co(NH_3)_6]Cl_3$ with $K_3[Co(CN)_6]$, rather than to be the hoped for $[Co(NH_3)_3(CN)_3]$.

The marked stability of the hexacyanocobalt(III) anion compared to species containing fewer cyanide ions co-ordinated per cobalt(III) is suggested by the literature of the cobalt(III) ammines. Although many compounds containing $[Co(CN)_6]^{3-}$ have been reported, $[Co(NH_3)_4(H_2O)(CN)]Cl_2$[2] and the salts of $[Co(en)_2(CN)_2]^+$[3] are the only cyanide-containing ammines of cobalt(III) reported.

RÂY[4] found that $[Co(NH_3)_5(S_2O_3)]Cl$ reacted with KCN to form $K_4[Co(CN)_5(S_2O_3)]$, and later ADAMSON[5] reported the analogous reaction for $[Co(NH_3)_5Br]^{++}$. The mechanism of the substitution was suggested by ADAMSON to consist of a rapid, cobalt(II)-catalysed path involving atom transfer and a slow reaction path not further identified. The slowness of the reaction of $[Co(NH_3)_6]Cl_3$ with NaCN suggests that the first step (slow) may be the replacement of one NH_3 to give the ion $[Co(NH_3)_5(CN)]^{++}$, which then undergoes a rapid "atom" transfer with $Co(CN)_5^{3-}$ to yield $[Co(CN)_6]^{3-}$ and $[Co(NH_3)_5]^{++}$ via the cobalt(II)-catalysed mechanism with NaCN given by ADAMSON for the rapid path in the reaction of $[Co(NH_3)_5X]^{++}$.

After this work had been completed, a brief report on the reaction of cobalt(III) ammines with cyanide ion appeared.[6] The results reported for the reaction of $[Co(NH_3)_6]^{3+}$ with cyanide are strikingly different from the present study in that the major product of the reaction was found to be an ion containing five cyanides per cobalt(III). Because of the absence of experimental details in the article, it is difficult to determine the cause for the difference in the course of the reaction in the two cases. One obvious difference is in the ratio of reactants, but this difference would appear on the surface to favour the formation of a pentacyano species more in the present study, for which there is less cyanide per cobalt. Another difference might be in concentrations; it appears that the solutions used by SHARPE and coworkers were at least tenfold more dilute than those used here. In a more dilute system the controlling step might be the aquation of $[Co(NH_3)_6]^{3+}$ rather than the replacement of NH_3 by CN^-. A pentacyano-cobalt(III) species could then result from a cobalt(II)-catalysed atom transfer.

The complete replacement of NH_3 by CN^- is also observed with platinum(II). BUCKTON[7] found that KCN reacts with $[Pt(NH_3)_4]Cl_2$ in aqueous solution to precipitate $[Pt(NH_3)_4][Pt(CN)_4]$. It is interesting to note that GRINBERG[8] reports an intermediate behaviour for the reactions involving thiocyanate in place of cyanide. In aqueous medium the expected $[Pt(NH_3)_2(SCN)_2]$ is isolated, but accompanied by some $[Pt(NH_3)_4][Pt(SCN)_4]$, whereas thermal decomposition of dry $[Pt(NH_3)_4](SCN)_2$ leads only to $[Pt(NH_3)_4][Pt(SCN)_4]$.

(1) H. TAUBE, *Chem. Rev.* **50**, 111 (1952).
(2) K. A. HOFMANN and S. REINSCH, *Z. Anorg. Chem.* **16**, 377 (1898).
(3) P. RÂY and B. SARMA, *J. Indian Chem. Soc.* **28**, 59 (1951).
(4) P. RÂY, *Quart. J. Indian Chem. Soc.* **4**, 325 (1927).
(5) A. W. ADAMSON, *J. Amer. Chem. Soc.* **78**, 4260 (1956).
(6) H. S. NAGARAJAIAH, A. G. SHARPE and D. B. WAKEFIELD, *Proc. Chem. Soc.* 385 (1959).
(7) G. B. BUCKTON, *Rec. Trav. Chim.* p. 393. Würtzburg, May 1851; *Chem. Zentr.* **22**, 696 (1851).
(8) A. A. GRINBERG, *Izv. Sektora Platiny i Drugikh Blagorod. Metal. Inst. Obshch. i Neorg. Khim.* No. 6, 122 (1928); A. A. GRINBERG and B. V. PTITSYN, *Ibid.* No. 9, 73 (1932).

Experimental

The general procedure was to add a solution of 3·0 g of NaCN in 10 ml H_2O dropwise with stirring to a solution of 5·35 g of $[Co(NH_3)_6]Cl_3$ (obtained from the G. F. Smith Chemical Co., Columbus, Ohio) in 100 ml of H_2O while maintaining the reaction mixture at the desired temperature. The amounts of precipitate formed were 0·12 g at 5°C, 0·68 g at room temperature (about 24°C), and 2·50 g at 80°C. (Found: Co, 31·3%; NH_3, 27·4%; N, 44·2%. Calc. for $[Co(NH_3)_6][Co(CN)_6]$: Co, 31·3%; NH_3, 27·2%; N, 44·7%).

The authentic $[Co(NH_3)_6][Co(CN)_6]$ was prepared by the reaction of $[Co(NH_3)_6]Cl_3$ with $K_3[Co(CN)_6]$, a procedure suggested in GMELIN[9]. The addition of 6·1 g of $K_3[Co(CN)_6]$ (prepared to a solution of 5·0 g of $[Co(NH_3)_6]Cl_3$ in 100ml of H_2O as described in *Inorganic Syntheses*[10]) dissolved in 150 ml of H_2O at room temperature gave a precipitate of 6·4 g of $[Co(NH_3)_6][Co(CN)_6]$. X-ray powder diffraction patterns of this product and the product of the reaction of $[Co(NH_3)_6]Cl_3$ with NaCN proved to be identical.

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[9] GMELINS *Handbuch der Anorganischen Chemie, Kobalt* Teil B. System Nummer 58, (8th Ed.) p. 70. Verlag Chemie, Berlin (1930).
[10] J. H. BIGELOW, *Inorg. Synth.* **2**, 225 (1946).

Simple laboratory preparation of anhydrous silver tetrafluoroborate

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AQUEOUS silver tetrafluoroborate can be prepared in the usual way after WILKE-DORFURT and BALZ[1] from silver carbonate and fluoroboric acid. However, it is not possible to dehydrate it without decomposition. Anhydrous silver tetrafluoroborate was first prepared by SHARPE[2] from silver metaborate and bromine trifluoride.

$$3AgBO_2 + 4BrF_3 \rightarrow 3AgBF_4 + Br_2 + 3O_2$$

WARF[3] has prepared a solution of the complex of toluene and silver fluoroborate in toluene by passing boron trifluoride into a suspension of silver fluoride in toulene under reflux. He found it impossible, however, to isolate the solid silver tetrafluoborate from this solution. Recently MEERWEIN and WUNDERLICH[4] used silver oxide and boron trifluoride in the preparation of anhydrous silver tetrafluoroborate

$$4AgO_2 + 8BF_3 \rightarrow 6AgBF_4 + 2AgBO_2.$$

Silver metaborate formed as by product makes further purification necessary. CLIFFORD and KONGPRICHA[5] on the other hand have developed a simple method using silver nitrate, HF and BF_3

$$AgNO_3 + HF + BF_3 \rightarrow AgBF_4 + HNO_3.$$

The removal of nitric acid from the product and handling of liquid HF represent preparative problems.

We have now found that it is possible to prepare anhydrous silver tetrafluoroborate simply by reacting commercially available silver (I) fluoride with boron trifluoride, in a suitable solvent such as nitromethane.

$$AgF + BF_3 \rightarrow AgBF_4$$

[1] E. WILKE-DORFURT and G. BALZ, *Z. Anorg. Chem.* **159**, 197 (1927).
[2] A. G. SHARPE, *J. Chem. Soc.* 4538 (1952).
[3] J. C. WARF, *J. Amer. Chem. Soc.* **74**, 3702 (1952).
[4] H. MEERWEIN and K. WUNDERLICH, *Angew. Chem.* **69**, 481 (1957).
[5] A. F. CLIFFORD and S. KONGPRICHA, *J. Inorg. Nucl. Chem.* **5**, 76 (1957).

To carry out the reaction the argentous fluoride is suspended in nitromethane and then boron trifluoride is introduced into the system. The solvent is then pumped off under vacuum. The silver fluoroborate is obtained as a white crystalline powder. It is very hygroscopic and somewhat light sensitive. It was found suitable to store it below pentane, which can be easily pumped off before use.

We further observed, that a nitromethane solution of anhydrous HF and BF_3, which acts as anhydrous HBF_4, is capable of slowly dissolving finely divided silver powder with formation of $AgBF_4$. This behaviour is in accordance with MEERWEIN's observation[6] that finely divided silver powder is dissolved by acetonitrile solutions of aryl diazonium tetrafluoroborates and triphenylmethyl carbonium tetrafluoroborate with the formation of $AgBF_4$.

Experimental

Thirty-four grammes (0·268 mole) of silver fluoride (Harshaw Chemical Company) was suspended in 40 g of dry nitromethane and boron trifluoride was passed into the shaken suspension for approximately 30 min. The apparatus was protected in the usual way from air moisture. The temperature of the system rose to 60°C and was maintained near that value by periodically dipping the reaction vessel into an ice bath. When the solid AgF had almost completely gone into solution. BF_3 addition was stopped. The quantity of BF_3 absorbed was 19·5 g (0·28 mole) (Theoretical quantity for complete reaction of AgF is 18 g.) The nitromethane solution of silver fluoborate was colourless but murky. Dry nitrogen was passed through this solution for 1 hr to remove some of the excess BF_3 present. The CH_3NO_2 solution was then filtered under dry nitrogen through a sintered glass disk into an evacuated flask held at a temperature of 70°C and under a pressure of approximately 5 mm. The filtered solution was completely clear. The evacuated flask was topped by an externally heated glass column which facilitated removal of the nitromethane which was collected in a liquid nitrogen trap. Upon removal of the solvent, an off-white solid remained which was covered in a dry box with n-pentane and ground in a mortar under this hydrocarbon to give a solid of small particle size. Normal pentane was employed to protect the solid from exposure to the atmosphere and because it could be very easily removed to give the dry solid by evacuation at atmospheric temperature. After grinding the fluoborate was pumped dry at 70°C and then stored under n-pentane. The weight of dry solid obtained was 46 g (0·237 mole, 88·5%). In view of the fact that grinding and other handling procedures resulted in physical losses of the product, it is apparent that based on the quantity of AgF employed, a yield of the order of 90 per cent was obtained.

($AgBF_4$ (194·7) Found: Ag, 56·05%. Calc.: Ag, 55·4%.)
(BF_4^- (as nitron salt) Found: 43·8%. Calc.: 44·6%).

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[6] H. MEERWEIN, V. HEDERICH and K. WUNDERLICH, *Arch. Pharm.* **291/63** 541 (1958).

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Preparation of pure pyrophosphorous acid

(*Received* 23 *March* 1960)

THIS note is prompted by a recent private communication from a European laboratory stating that phosphorus trihalides dissolve simply in orthophosphorous acid, in spite of AUGER's[1] claim to have made pyrophosphorous acid by violent agitation of a mixture of orthophosphorous acid and phosphorus trichloride with a current of carbon dioxide at temperatures near 35°C. Using nuclear magnetic resonance (N.M.R.) for analysis, we find that both phosphorus trichloride and phosphorus tribromide react quantitatively with orthophosphorous acid to give pyrophosphorous acid.

When various ratios of crystalline orthophosphorous acid and phosphorus trichloride are sealed into glass tubes and held at temperatures in the range from 25 to 100°C, it is found that the following reaction occurs stoicheiometrically:

$$5(HO)_2HPO + PCl_3 \rightarrow 3(HO)H(O)POP(O)H(OH) + 3HCl \qquad (1)$$

[1] V. AUGER, *C.R. Acad. Sci., Paris* **136,** 814 (1903).

With an excess of phosphorus trichloride over the stoicheiometry of the above equation, two phases are observed—one phase consisting of phosphorus trichloride, the other, of HCl dissolved in pyrophosphorous acid. Orthophosphorous, pyrophosphorous, and hydrochloric acids appear to be miscible, so that only one phase is found when five or more moles of $(HO)_2HPO$ are used per mole of PCl_3. To the precision of 1 per cent of the total phosphorus by N.M.R., phosphorus trichloride and ortho-phosphorous acid react completely, when these substances are combined. No study has been made of the possibility of detecting an equilibrium when a small amount of pyrophosphorous acid is dissolved in a large excess of anhydrous hydrochloric acid under pressure.

AUGER's experiments were repeated at 35° and 100°C using both phosphorus tribromide and phosphorus trichloride. When the stoicheiometry of equation (1) was followed, pyrophosphorous acid was formed in at least 99 per cent purity. Pyrophosphorous acid containing only traces of HCl can also be obtained by opening the sealed tube corresponding to the stoicheiometry of equation (1) at acetone–dry ice temperatures and allowing the HCl to escape upon warming to room temperature. We have found the melting point of pyrophosphorous acid to be 36°C.

Due to indirect spin–spin splitting the of phosphorus by hydrogen, two sharp resonance peaks of equal intensity are seen in the N.M.R. spectrum at −21 p.p.m. and +28 p.p.m. of the magnetic field (as referenced to 85 per cent orthophosphoric acid at 25°C). This demonstrates that the pyrophosphorous acid is a symmetrical molecule; and the fact that the observed resonances exhibit the same chemical shifts as do the resonance peaks for sodium pyrophosphite made by careful dehydration of monosodium orthophosphite proves the structure. The P-H indirect spin–spin splitting equals 0·40 Gauss, which is the same as the splitting observed in the N.M.R. pattern of orthophosphorous acid. Moreover, the N.M.R. chemical shift from the ortho- to the pyrophosphorous acids is 11 p.p.m.—a value which is about equal to the chemical shift when going from ortho- to pyro-phosphoric acids.

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Physico-chemical studies on mercurous molybdate

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THE precipitation of metal molybdates is affected by a number of factors, e.g. concentration of MoO_4, age, formation of polymers and hydrolysis. Therefore simple gravimetric and titrimetric methods fail to indicate the correct composition of the precipitated salt. Hence the present investigation was initiated.

Experimental

Solutions of A.R. Na_2MoO_4 and $Hg_2(NO_3)_2$ were prepared in conductivity water. The former were standardized as the quinoline complex[1] $MoO_4(C_9H_6ON)_2$; $Hg_2(NO_3)_2$ was standardized against NaCl potentiometrically. Conductivities were measured with a Kohlrausch Universal Bridge, using a headphone, and were corrected for the dilution effect.[2] Titrations were performed in both forward and reverse directions in aqueous and aqueous alcoholic media. Potentiometric titrations were performed with a bright platinum foil electrode in conjunction with a S.C.E. and Cambridge pH-meter. For amperometric titrations a 'Manual Polarograph' was used; measurements were made using a moving coil galvanometer and a dropping mercury electrode as cathode. Current values obtained after each successive addition of the titrant to the electrolysis cell were corrected for the dilution effect.[3] To suppress maxima in the C-V curves, 0·1 per cent gelatine was used, and to eliminate the migration component of the limiting current 1 M KNO_3 was used as the supporting electrolyte.

As the nature of the molybdate ion is a function of H^+ concentration, precipitation of molybdate is mainly governed by the pH of the solution, and it is interesting to study the conditions necessary

[1] R. NIERICKER and W. D. TREADWELL, *Helv. Chim. Acta* **29**, 470 (1946).
[2] G. CHARLOT and D. BEZIER, *Quantitative Inorganic Analysis* p. 293. John Wiley, New York (1957).
[3] I. M. KOLTHOFF and J. J. LINGANE, *Polarography* (2nd Ed.) p. 890. Interscience, New York (1952).

for precipitation of mercurous molybdate. Dilute solutions of mercurous nitrate free from mercuric ion are prepared in water only, as the presence of free nitric acid leads to the formation of polymolybdate ion. Following KUAN PAN *et al.*[4], and BEVAN[5] we have also, studied the titration curves for mineral acid and Na_2MoO_4 and have found that at pH 4–6 trimolybdate ion predominates over other species. We have obtained normal mercurous molybdate $Hg_2O{\cdot}MoO_3$ in this pH-range; as this is a highly insoluble compound, a small concentration of molybdate ion is sufficient to precipitate the normal salt. Our observations are in accord with the views of REMY[6] that usually normal molybdates are precipitated when polymolybdates might be expected.

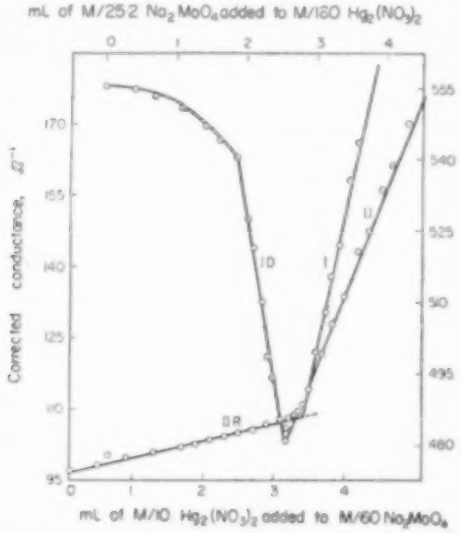

FIG. 1.—Conductimetric titration. Curve ID, direct titration; curve IIR, reverse titration.

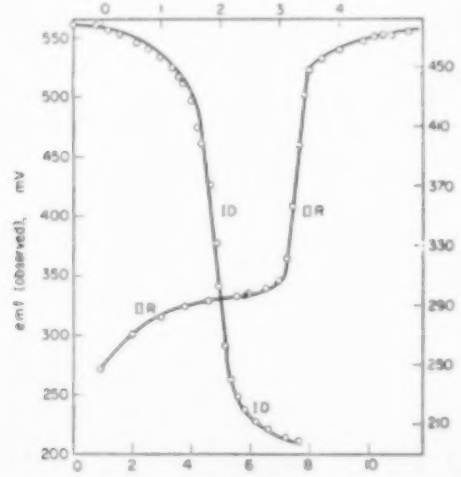

FIG. 2.—Direct and reverse potentiometric titration. Curve ID, 0·1M Na_2MoO_4 added to 20 cc of 0·025 M $Hg_2(NO_3)_2$: direct titration; curve IIR, 0·125 M $Hg_2(NO_3)_2$ added to 20 cc of 0·0166 M Ng_2MoO_4: reverse titration.

[4] KUAN PAN and T. M. HSEU, *Chem. Soc. Japan* **26**, 126 (1953).
[5] BEVAN, *Ann. Rep. Chem. Soc.* **53**, 53 (1943).
[6] H. REMY, *Treatise on Inorganic Chemistry* p. 168. Elsevier, London (1956).

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Fig. 1 (curves I and II) shows that the reaction between $Hg_2(NO_3)_2$ and Na_2MoO_4 may be followed conductimetrically. Both direct (I) and reverse conductivity curves (II) consist of two rectilinear branches with a sharp intersection at a point corresponding to the formation of mercurous molybdate Hg_2MoO_4, according to the following reaction

$$Hg_2(NO_3)_2 + Na_2MoO_4 \rightarrow Hg_2O{\cdot}MoO_3 + 2NaNO_3$$

The angle between the branches of the titration curves is very sharp. The changes in conductance can be explained on the basis of ionic mobilities. In alcohol, the results are improved slightly.

From Fig. 2 it may be seen that the reaction may also be successfully investigated with either of the reactants as the titrant. The equivalence point obtained from the maximum value of dE/dV and from the point of inflection in the curve occurs at a point corresponding to the formation of $Hg_2O{\cdot}MoO_3$.

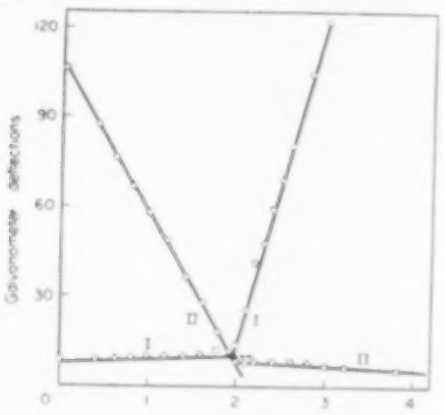

FIG. 3.—Amperometric titration. Curve I, ml of 0·05 M $Hg_2(NO_3)_2$ added to 5 ml Na_2MoO_4: reverse titration; curve II, ml of 0·05 M Na_2MoO_4 added to 10 ml $Hg_2(NO_3)_2$.

In direct titration (curve I), a precipitate initially separates but at the end-point, a sol appears to be formed. In reverse titration (curve II), the e.m.f. is slow to reach a steady value; the precipitate finally settles at the end-point, suggesting that the equivalence point has been reached. Alcohol and electrolytes such as KNO_3 and NH_4NO_3 have no effect on the end-point, nor on the nature of the curves.

Fig. 3 shows that the reaction can also be studied by amperometric titration, since one of the reacting substances shows a "polarographic diffusion current". At zero applied potential only the Hg_2^{++} ion, gives well-defined polarographic waves. In direct titration (curve II) the diffusion current decreases and reaches a minimum at the equivalence point, whereas in the reverse titration (curve I) no diffusion current is observed in the beginning; as the equivalence point is approached, the diffusion current increases linearly from almost zero. The results obtained by conductimetric, potentiometric and amperometric titrations are in concordance.

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A laboratory scale preparation of N_2F_4[1]

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DINITROGENTETRAFLUORIDE has been reported as a product of a reaction between NF_3 and certain solid metals.[2] When copper is used, temperatures near 375° and residence times in the order of 13

[1] This work was supported by the Office of Ordnance Research. Reproduction of all or part of this paper is permitted for any purpose of the United States Government.

[2] C. B. COLBURN and A. KENNEDY, *J. Amer. Chem. Soc.* **80**, 5004 (1958).

min are required. It appears that as the reaction proceeds, a protective copper fluoride coating is formed, which necessitates increasing the apparent reaction temperature and/or residence times with a corresponding decrease in the yield of N_2F_4. It has also been reported[3] that N_2F_4 has been prepared in small yields by the vapour phase fluorination of ammonia. An arc discharge process reported by FRAZER[4] converts NF_3 to N_2F_4 and N_2F_2 in the presence of mercury in substantial (51–67%) yields but the process is operated at 1–4 mm pressure and the production rate is slow.

In an attempt to find a suitable laboratory scale preparation of N_2F_4, NF_3 was found to react successfully with mercury in a flow system at between 320° to 330°. Temperatures outside of this range tended to lower the amount of desired product formed. For optimum results certain precautions, cited below, are necessary. Employing them, 60% of the NF_3 that reacted was converted to N_2F_4 and to a small amount of the so-called *cis* isomer of N_2F_2. The use of mercury as a reagent seems to have the following advantages over a solid metallic reagent: the metal fluoride formed, HgF_2 is less dense than and insoluble in mercury; gaseous NF_3 can be bubbled through the liquid phase; the residence time is lowered to about 30–60 sec; and the reaction is more homogeneous.

Certain obvious precautions are necessary. The reagents must be absolutely dry and free of impurities, especially oxygen-bearing substances. The NF_3 used in this work was prepared by the action of a D.C. current on a solution of pyridine in HF (Simons process). It was thoroughly scrubbed with aqueous solutions of KOH and KI and dried preliminarily with conc. H_2SO_4. It was further dried by passage through powdered P_2O_5 twice. Finally, it was thoroughly degassed. The mercury was redistilled.

The reaction system began with a cylinder of NF_3. This had a needle valve which controlled the flow of gas through a flow meter into a metal vessel containing the mercury. This vessel consisted of two sections. The lower section was made from 1 in. forged steel pipe 15 in. long. It had a flange at the top end. Just below the flange, on the outside of the pipe, were soldered several coils of $\frac{3}{8}$ in. copper tubing through which cooling water was passed. The upper section was constructed of 1 in. nickel pipe with a flange at the bottom. Through the top of this section was welded a $\frac{1}{4}$ in. nickel delivery tube and a like exit tube. When the two sections were assembled about a rubber gasket, the delivery tube reached to within $\frac{1}{4}$ in. of the bottom of the vessel. The outlet tube attached to a glass trap, in which the products were collected.

The reactor was heated with a fibrous glass heating tape wound about the lower 6 in. of the vessel. The reaction temperatures were determined by a thermocouple which was silver soldered to the vessel about $3\frac{1}{2}$ in. from the bottom.

This system, when assembled with the mercury in the reactor, was flushed with dried helium gas as the reactor was heated to 320° over a several hour period. A flow of NF_3 was then maintained, without a carrier gas, at a rate of about 8 g/hr. As the reaction began, a sudden rise in temperature was observed. A compensation was made for this, until thermal equilibrium was reached. At the end of the reaction period, the products were purged from the system with dry helium gas into the glass collection trap which was cooled with liquid air. The outlet arm of the glass trap had a tee through which a counter flow of dry helium gas was maintained to prevent atmospheric air and water from diffusing into the system. The reaction products were transferred *in vacuo* to the pot of a low temperature fractionating column. The head of the column was cooled with liquid air and a distillation was performed under an atmosphere of helium. The mixture of N_2F_2, N_2F_2, and NF_3 was allowed to warm slowly until liquid reflux was observed. This first condensate was slowly removed *via* a stop cock to a vacuum system and recondensed. As the least volatile component, N_2F_4, appeared in the reflux, it solidified on the head and was, in the main, retained there. Finally, when no further liquid reflux was in evidence, and the pot was empty, the solidified product was transferred to another collector in the vacuum system. It was a fluffy white solid which melted to a clear water white liquid. It had a mol. wt. of 103·5 and its infra-red spectrum was that reported for N_2F_4.[2]

If the first condensate fraction was slowly transferred *in vacuo* until a portion poor in NF_3 was retained, the residue was found to contain an undetermined amount of the so-called *cis* N_2F_2 on the basis of an infra-red spectrum.[5] This latter mixture of NF_3 and N_2F_2 was found to react with mercury and glass at room temperature. If a portion of the mixture was sealed *in vacuo* with some

[3] S. MORROW, D. PERRY and M. COHEN, *J. Amer. Chem. Soc.* **81**, 6338 (1959).
[4] J. W. FRAZER, *J. Inorg. Nucl. Chem.* **11**, 1166 (1959).
[5] C. B. COLBURN, F. JOHNSON, A. KENNEDY, K. MCCULLUM, L. METZGER and C. PARKER, *J. Amer. Chem. Soc.* **81**, 6397 (1959).

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glass fragments, the reaction produced a white solid and ultimately all the N_2F_2 was removed. On standing, the white solid that was produced slowly decomposed and evolved a brown gas with the properties of NO_2.

In a representative reaction between mercury and NF_3 using the conditions and precautions cited, 50 g of NF_3 were reacted with an initial charge of 616 g of Hg (48·5 ml). Essentially 14 g of NF_3 were recovered as such and 16 g of N_2F_4 were isolated.

The authors acknowledge their gratitude to Dr. C. B. COLBURN and his associates of the Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama, for the infra-red spectra of the various nitrogen fluorides compared in this work.

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The solubility of NaO_2 in liquid ammonia

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UP to the present time no particularly good solvents have been found for the alkali metal superoxides: however, these compounds are dissolved to a slight extent in liquid ammonia. An absorption spectrum of the O_2^- ion has been obtained for LiO_2, NaO_2 and KO_2 solutions,[1] and single crystals of NaO_2 were prepared for X-ray diffraction studies by recrystallization from liquid ammonia.[2] SCHECHTER and KLEINBERG have reported that NaO_2 is soluble in liquid ammonia to the extent of roughly 0·3 g/100 cc of solvent, with some decomposition.[3] Preliminary studies were performed in this laboratory by MONTABAN and SCHELAR[4].

In this work NaO_2(s) was placed in a removable Pyrex cup at the bottom of a 250 ml flask which was cooled by a dry ice-acetone slurry. The sample was separated from the flask proper by a fritted disk. Dry liquid ammonia was distilled off a Na–liquid NH_3 solution into the flask and submerged the NaO_2. The liquid NH_3 was stirred and allowed to stand for times ranging from 64 to 217 hr in order for equilibrium to be established between solid and dissolved NaO_2. The NH_3 was then forced over into a standard sulphuric acid solution to fix the amount of NH_3 and sodium in the resulting solution was determined by standard flame photometric methods.

The results of five runs at temperatures between -50° and -33°C failed to show any definite trend with temperature, and gave an average value for the solubility of 0·006 ± 0·002 g/100 ml of NH_3 or $1{\cdot}4 \times 10^{-3}$ g/mole of NH_3.

The superoxide was carefully handled in a dry atmosphere, and from X-ray and infra-red analyses showed 90–95 per cent superoxide with only small percentages of carbonate and hydroxide impurities. The samples were generously provided by the Callery Chemical Company through the courtesy of Dr. WILLIAM H. SCHECHTER.

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[1] J. K. THOMPSON and J. KLEINBERG, *J. Amer. Chem. Soc.* **73**, 1243 (1951).
[2] G. F. CARTER and D. H. TEMPLETON, *J. Amer. Chem. Soc.* **75**, 5247 (1953).
[3] D. L. SCHECHTER and J. KLEINBERG, *J. Amer. Chem. Soc.* **76**, 3297 (1954).
[4a] V. M. SCHELAR, M.S. THESIS, University of Wisconsin (1954); [4b] E. M. MONTABAN, B.S. Thesis, University of Wisconsin (1955).

Szilard–Chalmers reaction in metal phthalocyanines—II

(*Received* 14 *April* 1960)

IT has been reported that the effects of post irradiation heating on the retention of ^{65}Zn in neutron irradiated zinc phthalocyanine are anomalous.[1] When other metallic phthalocyanines such as the

[1] B. R. PAYNE, P. SCARGILL and G. B. COOK, *Radio-isotopes in Scientific Research* Vol. 2, p. 154. Pergamon Press, London (1958).

copper, cobalt and gallium derivatives were heated after irradiation, the retention increased (as do most other compounds exhibiting the Szilard–Chalmers effect) but the retention of the zinc compound appeared to decrease. This behaviour has been traced to a peculiarity of the method of extraction of the freed zinc ions from the irradiated zinc phthalocyanine. The method of extraction of the unretained metal ions consisted of refluxing the irradiated target with dilute sulphuric acid for 2 hr, filtering the solution and estimating the amount of radioactive metal in solid and solution. This gave reproducible results, (and as far as the copper, cobalt and gallium compounds were concerned, the expected ones for post irradiation heating) although it was known that the extraction was incomplete. Further experiments with the irradiated zinc compound, however, showed that the retention was quite low when determined by complete solution of the target in concentrated sulphuric acid, followed by dilution with ice water to precipitate the complex, but it increased slightly on post irradiation heating for 4 hr at 150 C, which is the normal behaviour in the circumstances. These results are shown in Table 1.

TABLE 1.—APPARENT RETENTION OF α- AND β-PHTHALOCYANINES

Form	Method of extraction	Apparent retention	
		No post irradiation heating	4 hr at 150 C
Znα-	Boiling dilute H_2SO_4	55·2[1]	26·0[1]
		57·6	23·7
α-	Solution in conc. H_2SO_4	9·1	12·0
		10·2	12·3
β	Boiling dilute H_2SO_4	97·3	97·8
		97·6	97·9
β	Solution in conc. H_2SO_4	12·1	16·0
		11·5	12·6
Cuα	Boiling dilute H_2SO_4	42·0	43·4
β	Boiling dilute H_2SO_4	83·9	91·0

Several factors which might have been responsible for the anomalous behaviour were also examined. To show that it was not due to the particular specimen of zinc phthalocyanine used earlier,[1] further material was prepared by the same method and also by double decomposition on mixing absolute alcoholic solutions of anhydrous zinc acetate and lithium phthalocyanine.[2] The zinc contents of both agreed with the theoretical value and infra-red analysis showed no free phthalocyanine.[3] Extraction by hot dilute sulphuric acid of the irradiated samples, with no post-irradiation heating and with 4 hr at 150 C, gave the same results as previously within the experimental error i.e. retention appeared to decrease.

Zinc phthalocyanine exists in two crystal modifications[3] (usually designated the α- and β-forms). A possible explanation therefore of the zinc anomaly was the conversion of one form to the other on post irradiation heating during which time the zinc atoms, freed by the Szilard–Chalmers recoil, were rejected by the lattice on conversion to the new crystal form with a reduced opportunity or none to combine subsequently. No data exists on the temperature at which this change occurs, but a thermal analysis using a simple differential arrangement showed that the α-form is converted to the β at about 130 C, i.e. below the temperature of the post irradiation heating used here. (The β-form appears to be stable.) However, copper phthalocyanine also exists in two modifications. The α-form of this has also been converted to the β-form by heating in this case at 200 C[4] although we found conversion to occur at 180 C. The β-form appears to be stable. Thus, a phase change also occurs

[2] P. A. BARRETT, D. A. FRYE and R. P. LINSTEAD, *J. Chem. Soc.* 1157 (1938).
[3] A. A. EBERT, JR. and H. B. GOTTLIEB, *J. Amer. Chem. Soc.* **74**, 2806 (1952).
[4] DR. GEORG VON LUSECH, FIAT Final Report No. 1313, Vol. III, *Dyestuff Research* p. 466. U.S. Department of Commerce, Washington D.C., (1948).

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in the copper compound at a temperature well below the maximum used for the post irradiation heating[1] (240 C) but no abnormality in retention was observed.

It can be seen from the table that the difference in retention between the α- and β-forms of zinc phthalocyanine is slight, when determined by the method of complete solution in strong sulphuric acid. There are large differences in apparent retention however, when dilute sulphuric acid is used to extract the recoil ^{65}Zn. This is probably due to differences in particle size as it is known that the α-forms have good covering power as pigments but the β-forms are useless.

Samples were examined by infra-red spectroscopy to determine their form,—previous work[1] was carried out with the zinc and copper in the α-form. The β-zinc compound for irradiation was prepared from the α- by boiling in acetone for 8 hr and the copper β-form, by boiling the α-modification in cyclohexanol for 4½ hr.[2] Radioactive ^{65}Zn was determined from the intensity of 1·17 MeV γ-ray peak by scintillation spectrometry, after ^{24}Na present in small amount as impurity had decayed.

I would like to thank Mr. P. J. Fydelor for the infra-red analyses.

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Absorption spectrum of Pm^{+3} in D_2O, DCl

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Three groups of investigators have already reported the general structure of the solution absorption spectrum in Pm^{+3} between 3000 and 10,000 Å.[1,2,3] In every case reported, the instrument employed was either a Model-LD or Model-DU Beckman spectrophotometer, and the largest amount of material handled was 5 mg.

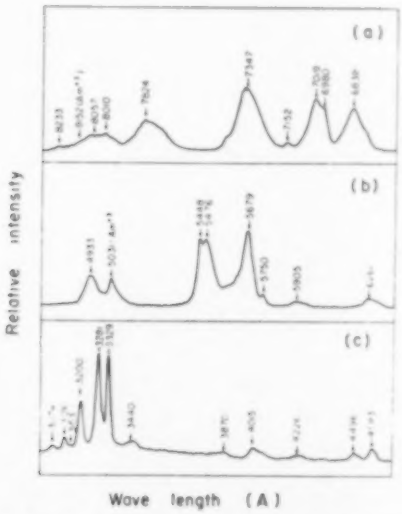

Fig. 1.—Solution absorption spectrum of 0·039 M Pm^{+3} in 0·023 M DCl (98% D_2O). (a) 6700 to 8300 Å; (b) 6300 to 4700 Å; and (c) 4700 to 3000 Å.

We wish to report the absorption spectrum of Pm^{+3} in 0·023 M DCl (98% D_2O) from 2600 to 19,000 Å under higher resolution than previously reported. Using a Cary Model-14 recording spectrophotometer, we have observed additional structure in the ultra-violet region. Molar extinction

[1] G. W. Parker and P. M. Lantz, *J. Amer. Chem. Soc.* **72**, 2834 (1950).
[2] W. F. Meggers, B. F. Scribner and W. R. Bozman, *J. Res. Nat. Bur. Stand.* **46**, 85 (1951).
[3] D. S. Stewart, Argonne National Laboratory Report, ANL 4812 (1956).

coefficients were calculated for all peaks from 2600 to 8233 Å. No additional peaks were observed from 8233 to 19,000 Å.

An emission-spectrum analysis of Pm^{+3} in 1 M HCl solution obtained from Oak Ridge National Laboratory indicated impurities of Nd, Sm, Al, Ca, and Am. Purification of 60 mg of Pm^{+3} was carried out by the use of a heated (87°C) Dowex-50 cation-exchange column with α-hydroxybutyric acid as eluting solution.[4] After all other rare-earth impurities were separated from Pm^{+3}, the column was converted to a 12 N HCl column and Pm^{+3} was separated from actinide impurities.[4]

TABLE 1.—ABSORPTION PEAKS OF Pm^{+3} IN 0·023 M DCl (98% D_2O)

λ, Wavelength of peak (Å)	Band width at half max. (Å)	Slit width (mm)	ε, molar extinction coefficient[a]
2610	–2690	0·080	—
3074	3056–3081	0·075	0·32
3126	3113–3139	0·061	0·77
3153	3147–3160	0·061	0·31
3200	3187–3213	0·061	2·53
3281	3268–3294	0·061	4·96
3329	3316–3342	0·061	4·73
3440	3413–3460	0·061	0·39
3870	3845–3890	0·030	0·21
4015	4000–4057	0·021	0·51
4226	4200–4250	0·017	0·20
4496	4472–4520	0·016	0·41
4583	4566–4600	0·015	0·69
4933	4890–4986	0·013	1·41
5448	5431–5470	0·012	3·40
5476	5470–5502	0·012	3·33
5679	5638–5700	0·013	3·77
5750	5726–5760	0·013	0·64
5905	5879–5929	0·013	0·23
6261	6226–6300	0·019	0·45
6838	6786–6886	0·048	2·13
6980	6962–7000	0·069	2·14
7019	7000–7036	0·071	2·54
7152	7128–7176	0·075	0·36
7347	7272–7400	0·13	3·05
7824	7725–7872	0·40	1·54
8010	7974–8046	0·52	0·85
8057	8046–8080	0·52	0·74
8233	8200–8245	0·71	0·24

(No other absorption peaks were seen to 1·89 μ)

[a] $\text{Log}\,(I_0/I) = A = \varepsilon bc$, where A is the absorbance, ε is in litres × cm^{-1} × $moles^{-1}$, b is the cell path length —2·001 cm, and c is in moles/l.

The $PmCl_3$ solution was then taken to complete dryness under a heat lamp, and 30 ml of DCl, D_2O solution added. The drying procedure was again repeated, and again new D_2O, DCl solution added, giving a final solution of $PmCl_3$ in D_2O, DCl.

The solution used in the absorption cells was analysed before and after each run. The concentration of Pm^{+3} was determined by 4π beta counting, and the chloride concentration by the Volhard

[4] R. M. DIAMOND, K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954).

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method. The amount of H_2O in the Pm^{+3} sample was obtained by comparison with known solutions of H_2O in the D_2O stock. One sample contained 30·0 mg Pm^{+3} per 5·23 ml 0·023 M DCl (98 % D_2O).

The Cary 14 spectrophotometer was calibrated at the factory with an AH4 Hg arc. The Nd^{+3} and Am^{+3} standards were run in this laboratory in order to check the absolute values of peak wavelengths. The calibration results indicated the instrument to be correct to 1·5 Å in the region from 2700 to 4900 Å and 2 Å from 4900 Å to 2 μ. The resolving power of the monochromator is about 1·0 Å in the ultra-violet and visible ranges and about 3·0 Å in the near infra-red. The wavelength scale is reproducible to 0·5 Å. Table 1 includes corrected wavelength values. The uncertainty in peak locations is ≤ 2 Å. Slit widths and molar extinction coefficients, ϵ, are also given.

The Pm^{+3} solution spectrum was compared with solution spectra of Eu^{+3}, Nd^{+3}, Sm^{+3}, and Am^{+3}. No trace of the rare-earth ions was observed. A trace of Am^{+3} was detected by α-assay (0·06 mg/ml). Consequently, the Am^{+3} peaks at 5033 and 8152 Å were subtracted from the promethium spectrum and the remaining peaks taken as Pm^{+3} peaks. The solution absorption spectrum is shown in Fig. 1.

Since additional peaks are not observed from 0·8 to 1·9 μ, the groundstate multiplets, $^5I_4$ to $^5I_8$, should be separated by less than 5400 cm^{-1}. The group of peaks around 8000 Å are probably due to transitions from $^5I_4$ to the ^5F and ^5S multiplets. However, an analysis of the Pm^{+3} spectrum is best undertaken by studying the ion in a solid matrix. Such studies have already begun.[5]

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[5] J. G. Conway and J. B. Gruber, Luminescence Spectrum of $PmCl_3$, UCRL-9042 (1960); *J. Chem. Phys.* **32**, 1586 (1960).

J. Inorg. Nucl. Chem., 1960, Vol. 14, pp. 306 to 310. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Approximate empirical formula for internal conversion coefficients

(*Received* 11 *February* 1960)

THE internal conversion coefficient is one of the important factors upon which the detection limit for a radionuclide depends when a γ-scintillation spectrometer is employed for detection.

This coefficient has been determined for a relatively small proportion of all γ-rays. About 448 values can be found in the *Table of Isotopes*[1] including cases where the internal conversion coefficients can be estimated from the related experimental data,[1] i.e. the observed values of e_K/γ, $e_K/(e_L + e_M)$, $e_K/e_{L_I}/e_{L_{II}}$, etc., where e_K represents the number of internal conversion electrons from K electron shell. This corresponds to only one tenth of all known γ-rays.

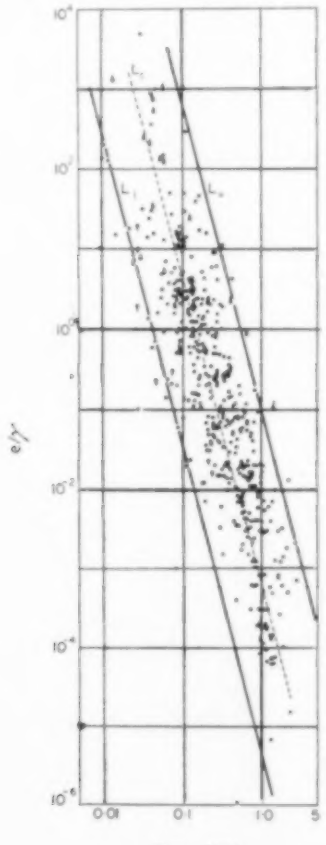

FIG. 1.—Plot of internal conversion coefficient against γ-energy.

[1] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).

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If the internal conversion coefficient is expressed as a function of the γ-energy using these experimental data, the coefficients for other γ-rays may be estimated to some extent. The coefficients for these 448 cases have been plotted against the γ-energy on log–log paper, and the centre line, L_c, has been found graphically. Further, equidistant thick lines L_u and L_l which are parallel to L_c have been drawn in such a way as 95 per cent of 448 points lie inside the lines, Fig. 1. From these lines a formula for internal conversion coefficients has been obtained as follows:

$$8{\cdot}3 \times 10^{-3} E_\gamma^{-2{\cdot}9} > e/\gamma > 3{\cdot}7 \times 10^{-6} E_\gamma^{-2{\cdot}9} \qquad (1)$$

and

$$(e/\gamma) \text{ most probable} = 5{\cdot}5 \times 10^{-4} E_\gamma^{-2{\cdot}9} \qquad (2)$$

The inequality (1) has a probability of 95 per cent.

Examples of the application of these formulae will be shown below. Since the energy of the γ-ray emitted from fluorine-20 (10·7 sec) is 1·63 MeV, the internal conversion coefficient for this γ-ray has a 95 per cent probability of lying between $1{\cdot}3 \times 10^{-2}$ and 5×10^{-7}. Since the branching ratio for this mode of decay is supposed to be unity, the fractional abundance of unconverted γ-photons must lie between 0·987 and 0·9999995. In the same way, it can be deduced, with the same probable error, that the fractional abundance of unconverted γ-photons for the γ-ray emitted from antimony-124*m* (21 min), whose γ-energy is 0·0185 MeV, is less than 0·04.

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Nickel nitrosyl complexes*

(*Received* 14 *April* 1960)

THE blue complexes formed by reacting nickel carbonyl with NO have been investigated by several authors.[1-6] However, what appear to be identical nickel species have been variously formulated as: $(NiNO)^-$ (see ref. 1); $(NiNO)^{+2}$ (see ref. 2) and $(NiNO)^{+2}$ (see ref. 6). The disagreement among these investigators appears to be due to the presence of oxidized impurities.

The present author has succeeded in preparing several stable complexes which are easily purified and whose properties can be rigorously investigated.

Calc. for $[(C_6H_5)_3P]_2NiNOBr$ (%)		Found (%)
C	62·35	62·48
H	4·36	4·71
P	8·93	8·88
N	2·03	2·00
Br	11·51	11·22
Ni	8·48	8·00
O	2·31	2·71*

* By difference; m.p. (vacuum) 203–209°; mol. wt. Calc.: 693; Found: 712

* This research was sponsored by the International Nickel Co. Inc., 67 Wall Street, New York 5, New York.

(1) J. S. ANDERSON, *Z. Anorg. Chem.* **229,** 357 (1936).
(2) W. P. GRIFFITH, J. LEWIS and G. WILKINSON, *J. Chem. Soc.* 1775 (1959).
(3) H. REIHLEN, A. GRUHL, G. VAN HESSLING and O. PFRENGLE, *Liebigs Ann.* **482,** 161 (1930).
(4) R. L. MOND and A. E. WALLIS, *J. Chem. Soc.* **121,** 32 (1922).
(5) J. C. W. FRAZER and W. E. TROUT, *J. Amer. Chem. Soc.* **58,** 2201 (1936).
(6) H. REIHLEN, *Z. Anorg. Chem.* **230,** 223 (1937).

Five grammes of $[(C_6H_5)_3P]_2NiBr_2$ were dissolved in 50 ml of tetrahydrofuran. To this solution was added 5·6 g of anhydrous $NaNO_2$. After refluxing for 30 min, the dark blue, almost black, solution was filtered and evaporated to a volume of 25 ml, and 25 ml of n-hexane was added. A small amount of a green oil separated out, from which the solution was decanted. On cooling the solution 1·3 g of the dark blue product precipitated and was filtered, washed and dried.

The infra-red spectrum shows the presence of a strong NO band at 1735 cm^{-1} while all the other infra-red frequencies down to 700 cm^{-1} are due to $(C_6H_5)_3P$. This is similar to the frequency of 1820 cm^{-1} reported by GRIFFITH *et al.*[1]

Several other compounds such as $(C_6H_5)_3PONNiOCH_2{\cdot}2CH_2OH$ have been prepared. These compounds will be reported in detail in the near future.

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Interhalogen complexes in aqueous solution

(*Received* 15 *April* 1960)

FAULL investigated the systems I_2–Br_2–Br^- and I_2–Cl_2–Cl^- by extraction of the neutral halogen into CCl_4.[1] He was able to interpret his results at 25° C in terms of the aqueous equilibria:

$$2IBr = I_2 + Br_2 \qquad (1)$$
$$K_1 = 1{\cdot}2 \times 10^{-4}$$

$$IBr + Br^- = IBr_2^- \qquad (2)$$
$$K_2 = 370$$

$$2ICl = I_2 + Cl_2 \qquad (3)$$
$$K_3 = 1{\cdot}62 \times 10^{-10}$$

$$ICl + Cl^- = ICl_2^- \qquad (4)$$
$$K_4 = 170$$

NEUMANN studied reaction (4) by measuring the ultra-violet absorption of ICl_2^- and roughly confirmed FAULL's results,[2] while in a recently completed study I have confirmed FAULL's findings in the IBr system, finding that equations (1) and (2) can explain to within a few per cent the distribution of IBr between CCl_4 and aqueous bromide solutions from 10^{-2} to 1 M in Br^-.[3] I have also elucidated the analogous reactions involving the heavier halogen astatine:[3]

$$AtI + I^- = AtI_2^-$$

and

$$AtBr + Br^- = AtBr_2^-.$$

In a paper published last year in this journal, PUNGOR *et al.* reported the results of potentiometric studies of the BrCl–Cl^-, ICl–Cl^- and IBr–Br^- systems which they interpreted to indicate that the complex ions formed were respectively $BrCl_4^-$, ICl_6^- and IBr_4^-.[4] Since these conclusions differ markedly from FAULL's, a re-examination of the potentiometric study seems in order.

PUNGOR *et al.* calculated their potentials from the couple: $X^- + Y^- = XY + 2e$, in which X is the more electropositive halogen of the interhalogen compound. They assumed the concentration

[1] J. H. FAULL, *J. Amer. Chem. Soc.* **56**, 522 (1934).
[2] H. M. NEUMANN, Paper presented at the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958; Division of Inorganic Chemistry, Abstract No. 84. (A misprint in the abstract gives $1/K_4$ as $1{\cdot}3 \times 10^{-2}$. The actual value found was $1{\cdot}3 \times 10^{-2}$.)
[3] E. H. APPELMAN, UCRL-9025 (Thesis.)
[4] E. PUNGOR, K. BURGER and E. SCHULEK, *J. Inorg. Nucl. Chem.* **11**, 56 (1959).

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of X^- to be constant. This is a manifestly incorrect assumption, since the X^- concentration is controlled by the equilibria:

$$XY + Y^- = Y_2 + X^- \tag{5}$$

and

$$2XY = X_2 + Y_2 \tag{6}$$

In a solution to which no excess of X_2 or Y_2 has been added, the form of the Y^- dependence of the emf depends on which of equations (5) and (6) proceeds further to the right. There are two limiting cases. If the Y_2 produced by (6) is negligible compared with that produced by (5):

$$E - E_0 = \frac{0{\cdot}058}{4} \log K_5 - \frac{0{\cdot}058}{4} \log \left[\frac{(XY)_{\text{total}}}{(Y^-)^2 + K_n(Y^-)^{n+2}} \right] \tag{7}$$

while if the reverse is true:

$$E - E_0 = \frac{0{\cdot}058}{2} \log K_6 - \frac{0{\cdot}058}{2} \log \left[\frac{(XY)_{\text{total}}}{(Y^-)^2 + K_n(Y^-)^{n+2}} \right] \tag{8}$$

Here E_0 is the standard potential of the aqueous Y_2–Y^- couple, E is the observed cell potential, K_5 and K_6 are the equilibrium constants of equations (5) and (6), respectively, and K_n is the equilibrium constant for the reaction

$$XY + (n-1)Y^- = XY_n^{1-n} \tag{9}$$

The value 0·058 has been used for $(RT/F \ln 10)$ instead of the 25° value of 0·0592 to conform with the usage of PUNGOR *et al.*

It is obvious that neither equation (7) nor equation (8) is equivalent to equation (2) of PUNGOR *et al.* except for the special case of $X \equiv Y$, e.g. for I_2, when equation (8) is exactly correct and does reduce to PUNGOR's equation (after the latter has been corrected for the obvious typographical error in the right-hand denominator).

From equations (1) and (3) and the standard I_2–I^-, Br_2–Br^- and Cl_2–Cl^- potentials,[5] we may calculate K_5 to be 1×10^{-15} for ICl and 4×10^{-11} for IBr. Using equations (1) through (6) we may then compute that in all of the ICl systems of PUNGOR *et al.* reaction (6) proceeds to the right much more than does reaction (5). Reaction (6) also predominates in most of the IBr systems, though the two become comparable at the highest Br^- concentrations. Data are not available for evaluating the relative importance of reactions (5) and (6) for the BrCl systems.

The most accurate way of determining n from the potentiometric data is to plot e.m.f. vs. log (Y^-). At sufficiently high (Y^-) the first terms in the denominators of equations (7) and (8) become negligible, and the plot becomes linear, its slope being a function of n. I have made such plots from the data of PUNGOR *et al.* The resulting n values, calculated by equation (8), appear in Table 1. Correction has been made for bound Y^- on the assumption that $n = 2$. A greater correction would lower the value of n determined from the plot.

When activity corrections are indicated, they have been made using the tabulated activity coefficients of HCl, with the assumption that the salting of I_2 from aqueous solution by $HClO_4$ is a good measure of the change in activity of XY with increasing HCl concentration,[6] and with the further assumption that $n = 2$ and that therefore the salt effect of HCl on equation (9) is the same as that of $HClO_4$ on the reaction $I_2 + I^- = I_3^-$.[6] If $n > 2$, exact activity corrections would lower the n values obtained from the curves.

The discrepancy between this work and FAULL's would therefore seem to be largely resolved, particularly if we regard the n values for the I_3^- systems as indicative of the accuracy of the potentiometric work. The expected value of n for I_3^- is, of course, 2·0.

The agreement between experimental and calculated potentials in Tables 1 to 4 of the paper by PUNGOR *et al.* is striking. However, I have been utterly unable to reproduce their "calculated" values. They seem to have neglected the relatively large amount of Y^- which must be bound into complex ions if their values of n are correct, but even aside from this the calculated potentials do not show the (Y^-) and $(XY)_{\text{total}}$ dependences which one would calculate from their equation (2), using their n and K_n values. For example, $dE/d \log (XY)_{\text{total}}$ should be 0·029 instead of the values 0·06 to 0·08 shown by the "calculated" potentials.

[5] W. M. LATIMER, *The Oxidation States of the Elements*. Prentice-Hall, New York (1952).
[6] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **77**, 5814 (1955).

TABLE 1

XY	$(XY)_{Total}$	n
BrCl	0·05	4·7[a]
	0·005	4·3[a]
	0·05[b]	3·0[b,c]
	0·005[b]	2·5[b,c]
ICl	0·02	2·9[a]
	0·01	3·5[a]
	0·02[b]	2·3[a,b]
	0·01[b]	2·7[a,b]
IBr	0·02	2·4
	0·01	2·2
I_2	0·02	1·4
	0·01	1·4

[a] At the lowest Cl^- concentrations the plots curved toward lower values of n.
[b] These plots were corrected for activity changes.
[c] Relatively severe scatter was observed.

In addition to the interpretive errors in this study, the experimental procedure itself was not conducive to the obtaining of accurate results. The concentrations of X_2 and Y_2 produced by reactions (5) and (6) were extremely small. Thus quantities of X_2 and Y_2 which were formed by oxidation or reduction of the XY by impurities, or which were present due to imperfect stoicheiometry could easily become quite important, and the oxidation potentials of the solutions were therefore not under adequate control. It would be much more satisfactory to carry out the studies with solutions containing comparable concentrations of X_2 and XY. The relative importance of equations (5) and (6) would no longer be important since the Y_2 concentration would be fixed by equation (6), and the potential would be unequivocally determined. The minor complications resulting from such complexes as X_2Y^- could easily be resolved by additional experiments in the X_2–X^-–Y^- system.

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A list of some of the papers to be published in future issues

J. E. GINDLER, K. F. FLYNN and J. GRAY, JR.: Thermal neutron fission cross-section of ^{229}Th.

C. J. ORTH and R. K. SMITH: Short-lived isotopes of Nb and Zr from fission.

I. G. ALMEIDA and L. MARQUEZ: A method for the enrichment of radioisotopes produced by (γ, n).

J. MACKIN, P. ZIGMAN, D. LOVE, D. MACDONALD and D. SAM: Radiochemical analysis of individual fallout particles.

I. G. CAMPBELL: The effect of amine scavengers on products of neutron irradiation of organic halides

I. G. CAMPBELL: Some properties of the unstable intermediate produced by isomeric transition or n, γ reaction in bromates.

H. YAMATERA: Charge-transfer spectra in metal complexes, especially in halogenopentammine-cobalt(III) ions.

R. H. HOLM and F. A. COTTON: Dipole moments and structures of some bis-(trifluoroacetylacetonate) complexes.

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